Suppressing exciton deconfinement and dissociation for efficient thermally activated delayed fluorescence OLEDs

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ABSTRACT

The efficiency of organic light-emitting diodes that utilize the principle of thermally activated delayed fluorescence (TADF) depends sensitively on the host material in which the TADF emitter molecules (guests) are embedded. Potential loss processes are “deconfinement,” the transfer of excitons from the guest to the host, and “dissociation,” the formation of intermolecular charge-transfer states. We investigate how both processes can be suppressed by studying the photoluminescence efficiency, emission spectrum, and time-resolved emission intensity of eight thin-film systems in which 5 mol. % of the sky-blue TADF emitter 4-carbazolyl-methylphthalimide (abbreviated here as CzPIME) is embedded in various host materials. Deconfinement is found to be entirely suppressed if the triplet energy of the host is 0.25 eV or more above that of the guest. For systems allowing for deconfinement, the dependence on the energy difference is consistent with a recent theoretical analysis [C. Hauenstein *et al.*, J. Appl. Phys. **128**, 075501 (2020)]. Dissociation, due to hole transfer to a host molecule, is found to be suppressed if the host’s highest occupied molecular orbital energy is not more than about 0.2 eV higher than that of the guest. Otherwise, we observe an efficiency loss, a spectral redshift, and the disappearance of distinct prompt and delayed emission regimes. A comprehensive rate-equation model is developed from which we study the sensitivity of these observations to the energy level structure, the intermolecular interaction rates, and the photophysical rates that follow from a fit to the experimental data for the CzPIME:TCTA [tris(4-carbazoyl-9-ylphenyl)amine] system.

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I. INTRODUCTION

Displays that are based on organic light-emitting diodes (OLEDs) have developed as a competitive technology for hand-held devices and more recently also for large televisions.¹ Finding the optimal combination of materials remains challenging and a topic of ongoing research. We focus in this work on OLEDs that utilize the principle of thermally activated delayed fluorescence (TADF).^{2–6} Currently, intensive research on TADF OLEDs aims, in particular, at developing blue-emitting devices that combine high efficiency with a long operational lifetime.^{7–9} The emissive layer

(EML) of TADF-based OLEDs consists, in general, of a small concentration of emissive guest molecules that are embedded in a host material. At small guest concentrations, exciton diffusion is reduced so that efficiency losses due to concentration quenching can be prevented.¹⁰ Furthermore, embedding of the TADF emitter molecules in a host material or in multiple host materials (mixed matrix OLEDs) provides options for obtaining an improved balance of the effective electron and hole mobilities in the EML. These can be utilized to obtain a more uniform emission profile across the EML, leading to a reduced efficiency loss at high current densities (“roll-off”) and to an enhanced operational lifetime.¹¹

To realize these properties for a given TADF emitter, choosing the best-suited host material among the many hosts available from OLED research is a critical and non-trivial task.⁵ Some of the requirements for a good host material are intrinsic properties such as a high thermal and morphological stability and a large bond dissociation energy. Other requirements depend on the specific TADF emitter that it will be combined with. First, the triplet energy should be sufficiently high so that triplet exciton transfer from the guest to the host (“deconfinement”) is prevented. Second, the difference between the frontier orbital energies of the two materials should prevent the formation of intermolecular charge-transfer (CT) states between a guest and a host molecule (“dissociation”).^{12–15}

Figure 1 gives a schematic view of both processes. In panel (a), we show the lowest singlet and triplet excited states of both TADF emitter and host material. The rate of triplet exciton deconfinement is expected to depend on the triplet confinement energy barrier $\Delta E_T \equiv E_{T,h} - E_{T,g}$, with $E_{T,h}$ and $E_{T,g}$ being the host and guest triplet energies, respectively. Panel (b) depicts dissociation of a guest-exciton by hopping of a hole away from the TADF emitter and to a neighboring host molecule. Also shown in the figure is the possibility of the hole hopping to even farther away host molecules. The dissociation rate is determined, in part, by the energy barrier $\Delta E_{HOMO} \equiv E_{HOMO,g} - E_{HOMO,h}$ between the highest occupied molecular orbital (HOMO) energies $E_{HOMO,g}$ and $E_{HOMO,h}$ of the guest and the host, respectively. The dissociation rate further depends on the difference in binding energies between the exciton and the dissociated state, as will be discussed later in the paper [see Eq. (2)]. Exciton dissociation by a hop of an electron is energetically unfavorable for the host–guest systems studied in this work due to the high lowest unoccupied molecular orbital (LUMO) energies of the host materials.

We study the sky-blue TADF emitter 4-carbazolyl-methylphthalimide (CzPIME) in various often-used host materials. TADF OLEDs based on carbazole-phthalimide type donor-acceptor

molecules, with the HOMO located on the carbazole donor group and the LUMO located on the phthalimide acceptor group, have been studied extensively.^{16–24} The emission color can be varied from approximately 440 to 520 nm by replacing the methyl group with more extended substituents, by adding substituents to the carbazole group, or by combining the acceptor with two carbazole groups.²⁴ At low current densities, an external quantum efficiency (EQE) of about 23% has been realized.¹⁷ Devices based on enantiomeric derivatives have been found to show circularly polarized electroluminescence with a maximum EQE close to 20%.¹⁹

In this paper, we investigate how for CzPIME the deconfinement and dissociation of excitons can be recognized from the photoluminescence (PL) efficiency in combination with steady-state and time-resolved PL measurements. For some of the chosen CzPIME:host combinations, we observe deconfinement, characterized by a reduced PL efficiency and delayed fluorescence intensity. For other CzPIME:host combinations, we observe dissociation, also leading to a strong reduction of PL efficiency but in combination with redshifted emission from the CT-states. These processes are found to occur beyond critical threshold values for ΔE_T and ΔE_{HOMO} , respectively.

In recent work, we have focused on TADF host–guest systems showing only triplet exciton deconfinement and have concluded from kinetic Monte Carlo (KMC) simulations with the software Bumblebee that ΔE_T should be larger than 0.2 eV in order to fully prevent that process.^{25–27} Here, we investigate the validity of that design rule experimentally. Furthermore, we include a rate-equation-based modeling study of the systems showing exciton dissociation in order to rationalize the experimental threshold values and show how both processes affect the time-dependence of the PL intensity.

The paper is structured as follows: In Sec. II, an overview of all selected materials and their characteristic parameters is given. In Sec. III, the measured emission spectra, PL efficiency, and time-

FIG. 1. (a) Extended Jablonski diagram of the first singlet and triplet excited states, S_1 and T_1 respectively, on both the TADF guest and the host material. The arrows indicate the (non-)radiative singlet/triplet decay rates $k_{(n)r,S/T}$ and the (reverse) intersystem crossing rates $k_{(r)ISC}$ of the guest-exciton as well as the non-radiative triplet decay rate on the host $k_{nr,T,h}$. In red, triplet deconfinement is schematically depicted, depending on the confinement barrier $\Delta E_T = E_{T,h} - E_{T,g}$. (b) HOMO and LUMO energy levels of host and TADF guest, with a dissociation barrier $\Delta E_{HOMO} = E_{HOMO,g} - E_{HOMO,h}$ shown in red. In this case, the energetic barrier is negative, as it is more favorable for the hole to reside on the host. The hole can then also hop to even farther away host sites.

resolved PL decay curves are presented for all host–guest combinations. In Sec. IV, these results are analyzed using KMC simulations and rate-equation modeling depending on the host interactions. First, in Sec. IV A, we determine for which hosts no detrimental interaction occurs so that the emitter performs optimally, allowing for characterization of the intrinsic emitter properties. In Sec. IV B, we identify hosts showing deconfinement and use KMC simulations to study the transient PL decay behavior, discussing especially the complexities of determining the appropriate confinement energy barrier ΔE_T . Section IV C discusses the host materials allowing for dissociation. We use rate-equation modeling to understand the transient intensity decay, the relative contributions from TADF emission and CT-state emission, and the overall emission efficiency. Section V contains a summary and conclusions.

II. MATERIAL SELECTION AND CHARACTERIZATION

The molecular structures of all materials used in this study are shown in Fig. 2(a). They have been selected to cover a wide range of triplet and HOMO energies and as a result varying ΔE_T and ΔE_{HOMO} with respect to the CzPIME emitter. An overview of these parameters is included in the first five columns of Table I, which also contains the full names of all host materials. All values for ΔE_{HOMO} and for ΔE_T are shown in descending order in Figs. 2(b) and 2(c), respectively. Figure 3 shows how the PL efficiency is strongly correlated with the critical parameters for dissociation and deconfinement and marks the different regimes that can be distinguished.

The HOMO energies in Table I were obtained from Ultraviolet Photoelectron Spectroscopy (UPS), as described in Secs. S1 and S2 of the supplementary material. The tabulated values are determined from the onset energies of the UPS spectrum. The actual adiabatic HOMO energy differs, in general, slightly from the onset value due to the energetic disorder, vibrational relaxation, and the surface sensitivity of the experiment.²⁸ We expect that the uncertainty in E_{HOMO} is about 0.1–0.2 eV for all materials.

The tabulated triplet energies E_T for the host materials are peak values, obtained from low temperature phosphorescence measurements in the references also given in Table I. When possible, measurement results determined from evaporated thin films are reported. However, such experimental data were not available from the literature for all host materials. In those cases, values measured in frozen solution are taken instead.

III. PHOTOLUMINESCENCE EXPERIMENTS

A. PL spectra and PL efficiency

For all host materials, PL experiments were carried out on CzPIME:host (5 mol%) films with a thickness of 100 nm, deposited on a quartz substrate by thermal evaporation. Figure 4(a) shows the room temperature steady-state emission spectra in an integrating sphere, with excitation at 340 nm. For most hosts, the peak energy is 2.50–2.53 eV (peak wavelength 480–490 nm), corresponding to CzPIME emission. The full width at half maximum is 0.50 eV (95 nm) and the onset energy is around 2.90 eV (427 nm). The peak energy and its shift are given in the last two columns of Table I. For some of the materials, absorption might occur on the

FIG. 2. (a) The molecular structures of the TADF emitter CzPIME and the eight host materials used in this study. (b) The HOMO energies E_{HOMO} of all host materials in descending order, as well as that of the emitter. All E_{HOMO} values were obtained from UPS experiments (see Secs. S1 and S2 of the supplementary material). (c) The triplet energies E_T of all host materials, also in descending order, as well as that of the emitter. The sources for E_T are given in Table I.

host molecules, but the absence of host emission at higher energy in all cases shows that the exciton transfer to the guest is very efficient. The CzPIME emission energy is expected to depend on the polarizability of the host material. The relatively high peak energy of 2.53 eV for emission from CzPIME in CzSi could indicate that this host might be less polarizable than the materials for which the emission peak is closer to 2.50 eV. For TCTA and TAPC as hosts, the peak emission was found to be significantly redshifted. We regard these redshifts as an indication of dissociation and subsequent CT-state emission (see Sec. IV C).

The CzPIME phosphorescence spectrum in CzSi was measured in gated PL experiments with a 500 ms time delay at 77 K. As shown in Sec. S3 of the supplementary material, the peak and onset energies are 2.54 and 2.89 eV, respectively.

The PL efficiency, η_{PL} , was obtained by the de Mello method using an integrating sphere and three time-integrated measurements to account for self-absorption and re-excitation: (i) without

TABLE I. Overview of the HOMO and triplet energies for the emitter and the eight host materials, the host–guest HOMO energy difference ΔE_{HOMO} , and the triplet confinement energy ΔE_T . The PL efficiency η_{PL} , the peak emission energy $h\nu_{\text{peak}}$, and the peak shift $\Delta h\nu_{\text{peak}}$ obtained from steady-state PL experiments for 5 mol. % thin films are shown. Due to insufficient absorption of the sample, no PL efficiency could be determined for the DPEPO host–guest system.

Material	E_{HOMO} (eV)	ΔE_{HOMO} (eV)	E_T (eV)	ΔE_T (eV)	η_{PL}	$h\nu_{\text{peak}}$ (eV)	$\Delta h\nu_{\text{peak}}$ (eV)
CzPIMe	−6.17	...	2.54 ^a	...	...	...	...
TAPC ^c	−5.29	−0.88	2.87 ^{a29}	0.33	0.07	2.17	−0.33
TCTA ^d	−5.70	−0.47	2.83 ^{b30}	0.30	0.15	2.37	−0.13
CzSi ^e	−5.95	−0.22	3.02 ^{b31}	0.48	0.65	2.53	0.03
CDBP ^f	−6.06	−0.11	2.79 ^{a32}	0.25	0.61	2.50	~0
mCBP ^g	−6.09	−0.08	2.75 ^{a15}	0.21	0.62	2.50	~0
TPBi ^h	−6.13	−0.04	2.67 ^{b33}	0.12	0.32	2.50	~0
TAZ ⁱ	−6.69	0.52	2.70 ^{b34}	0.16	0.40	2.49	~0
DPEPO ^j	−6.79	0.62	2.99 ^{b35}	0.45	...	2.51	~0

^aDetermined from the evaporated thin film.

^bDetermined from frozen solution.

^c4,4′-Cyclohexylidenebis[*N,N*-bis(4-methylphenyl)benzenamine].

^dTris(4-Carbazoyl-9-ylphenyl)amine.

^e9-(4-Tert-Butylphenyl)-3,6-bis(triphenylsilyl)-9H-carbazole.

^f4,4′-Bis(9-carbazoyl)-2,2′-dimethylbiphenyl.

^g3,3-Di(9H-carbazol-9-yl)biphenyl.

^h2,2,2-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole).

ⁱ3-(Biphenyl-4-yl)-5-(4-tert-butylphenyl)-4-phenyl-4H-1,2,4-triazole.

^jBis[2-(diphenylphosphino)phenyl] ether oxide.

a sample, (ii) with indirect excitation of the sample, and (iii) with direct excitation.³⁶ As shown in Table I, η_{PL} was found to vary from about 7% for CzPIMe in TAPC to 60%–65% for CzPIMe in CzSi, CDBP, and mCBP.

FIG. 3. Overview of the confinement ΔE_T and dissociation ΔE_{HOMO} energy barriers with the respective PL efficiency of CzPIMe:host (5 mol. %) thin films. The gray dashed lines separate the groups of materials for which the respective processes occur. Due to insufficient absorption of the sample, no PL efficiency could be determined for the DPEPO host–guest system.

B. Time-resolved PL experiments

Figure 4(b) shows the time-resolved PL intensity of all host–guest systems after excitation with 375 nm and collected at 530 nm for TAPC and at 480 nm for all other hosts at room temperature. Three qualitatively different scenarios can be distinguished: Embedding in DPEPO, CzSi, and CDBP leads to extremely similar decay transients, with a prompt lifetime of about 5×10^{-8} s and a delayed lifetime of about 10^{-5} s with a ratio of the integrated delayed and prompt intensities of 6.45 (more detailed analysis in Sec. IV A). Embedding in mCBP, TAZ, and TPBi leads to emission with a decreased intensity of the delayed component. The emission in TCTA and TAPC does not show any distinct prompt and delayed components at all.

IV. ANALYSIS

Based on the photophysical data, we will discuss the three different scenarios in more detail in Subsections IV A–IV C: (A) systems in which no triplet deconfinement or dissociation takes place, (B) systems showing triplet deconfinement, and (C) systems showing exciton dissociation.

A. No deconfinement or dissociation

The CzPIMe:host (5 mol. %) thin films show no signs of exciton deconfinement or dissociation for CzSi, CDBP, and DPEPO as hosts. For the first two of these, similar and high values of the PL efficiency in the range of 60%–65% were found. No PL efficiency could be determined in DPEPO because of insufficient absorption due to its large energy gap. However, due to the extremely similar transient PL decay, the typically excellent

FIG. 4. (a) Emission spectra of 5 mol.% CzPIME:host thin films, measured under steady-state conditions with 340 nm excitation. The measured PL efficiency is also given in the legend. (b) Normalized time-resolved PL intensity of these films, collected at 530 nm for TAPC and 480 nm for all other hosts. The typical bi-exponential TADF behavior is observed in all but two hosts (TCTA and TAPC), which is discussed in Sec. IV C. The deviation of the delayed intensity in mCBP, TAZ, and TPBi from that in CzSi, CDBP, and DEPO is discussed in Sec. IV B.

performance of DPEPO as host for many TADF emitters, and the high energetic barriers for both processes (see Fig. 3), we are confident to place DPEPO in this host category (no deconfinement and no dissociation). Deconfinement is expected to lead to a reduced delayed emission intensity with a possibly enhanced delayed lifetime (depending on the triplet lifetime on the host).²⁶ Triplet quenching on the host could then reduce the PL efficiency. However, for the CzSi-, CDBP-, and DPEPO-based films, such evidence of deconfinement is not observed. Dissociation and the

formation of intermolecular CT-states are expected to lead to a red-shifted emission and a decrease in the PL efficiency. That is also not the case for these three systems. The absence of detrimental host interactions is consistent with the $(\Delta E_{\text{HOMO}} - \Delta E_{\text{T}})$ diagram in Fig. 3.

Having established that for these three systems excitons on CzPIME show neither deconfinement nor dissociation, we fit the transient PL decay to obtain the intrinsic photophysical rates of the TADF emitter indicated in Fig. 1(a). We use the analytical expressions for the time-dependent exciton populations given in Ref. 26 in combination with the logarithmic weighting of the fit residuals and restriction of the dataset described in Ref. 37. The radiative (“phosphorescence”) triplet decay rate $k_{\text{r,T}}$ is assumed to be zero since the spin-orbit coupling of the emitter is expected to be very small.

As a result of the extremely similar PL decays, the fit describes all three non-interacting host-guest systems in CzSi, CDBP, and DPEPO equally well. Even so, the fits do not enable us to distinguish whether any non-radiative decay is occurring from the singlet or the triplet state, or a combination of both. The reason is that due to the large ISC rate, the ratio between the singlet and triplet excitons is established soon after the start of the experiment and then remains equal to $k_{\text{ISC}}/k_{\text{r,ISC}}$ independent of time. In Table II, we therefore give fit results based on two different scenarios for the non-radiative decay. For fit I, non-radiative losses can occur from the singlet state but the non-radiative triplet decay rate is assumed to be zero. For fit II, the non-radiative rates from singlet and triplet states are assumed to be equal. Fit I describes the scenario for which non-radiative triplet decay (to the S_0 ground state) is regarded as a strictly spin-forbidden process, whereas within fit II this spin-restriction is assumed to be less limiting. Both scenarios result in a fit of the form

TABLE II. Characteristics of the time-resolved PL decay of 5 mol.% CzPIME in CzSi, with the prompt and delayed decay rates k_{p} and k_{d} , respectively, as well as the prompt intensity onset A and the PL efficiency η_{PL} . The photophysical rates for CzPIME obtained from rate-equation modeling (see Sec. IV A) of those characteristics, with $k_{(\text{n})\text{r,S/T}}$ being the (non-)radiative singlet/triplet decay rates and $k_{(\text{r})\text{ISC}}$ being the (reverse) intersystem crossing rates. For fit I, the non-radiative triplet decay rate is assumed to be zero and for fit II the non-radiative singlet and triplet decay rates are assumed to be equal. Both fit scenarios for the photophysical rates lead to exactly the same prompt and delayed decay rates, the same ratio of the integrated delayed and prompt intensities (6.45 for $A = 0.974$) and PL efficiency. The radiative decay rate of triplets (phosphorescence) is assumed to be zero.

Characteristics of the measured decay			
k_{p}	k_{d}	A	η_{PL}
$4.55 \times 10^7 \text{ s}^{-1}$	$1.90 \times 10^5 \text{ s}^{-1}$	0.974	0.65
Fitted photophysical rates (10^6 s^{-1})			
	Fit I	Fit II	
$k_{\text{r,S}}$	4.07	4.07	
$k_{\text{r,T}}$	0	0	
$k_{\text{nr,S}}$	2.19	0.073	
$k_{\text{nr,T}}$	0	0.073	
k_{ISC}	38.0	40.19	
k_{rISC}	1.38	1.30	

$I(t) = A\exp(-k_p t) + (1 - A)\exp(-k_d t)$, with an intensity onset A and prompt and delayed decay rates, k_p and k_d , that are given in Table II. As shown in Sec. S4 of the [supplementary material](#), the fit is excellent up to approximately 10^{-5} s. Both fits I and II reproduce the experimental observation of $\eta_{PL} = 0.65$ for CzSi. For fit I, where there are no losses from the triplet state, $k_{nr,S}$ is a factor $\sim k_{ISC}/k_{rISC}$ larger, matching the expected difference in exciton populations. Despite not being distinguishable from experiment, in Secs. IV C 4 and IV C 5, we find a significant impact of the different non-radiative rates for the case of CT-state formation. The other rates $k_{r,S}$, k_{ISC} , and k_{rISC} are almost equal for both fit scenarios and well within the typical range for donor-acceptor type TADF emitters.^{2,37} The slightly higher value of η_{PL} for CzPIME in CzSi is within the expected sample-to-sample variation of the PL efficiency for such systems.

B. Deconfinement

For CzPIME: host (5 mol. %) thin films with mCBP, TPBi, and TAZ as hosts, the delayed emission intensity is seen to be significantly smaller than in CzSi, CDBP, and DPEPO. However, the emission spectrum is very similar. Based on the previous work, we regard the decreased delayed intensity as a signature of triplet deconfinement.²⁶ The clear distinction between the prompt and delayed contributions indicates that the coupling between the triplet states on the host and guest molecules is relatively strong and that the host triplet diffusion coefficient is relatively large. Under those conditions (“fast-diffusion limit”),²⁶ the reduction of the intensity onset of the delayed fluorescence component is equal to $P_{T,g}$, the probability that a triplet in the host-guest system resides on a guest molecule. From the Boltzmann statistics, $P_{T,g}$ is given by

$$P_{T,g} = \frac{c_g}{c_g + c_h \exp\left[-\frac{\Delta E_T}{k_B T} + \frac{\sigma_{T,h}^2 - \sigma_{T,g}^2}{2(k_B T)^2}\right]}, \quad (1)$$

where c_h and $c_g \equiv (1 - c_h)$ are the host and guest concentrations, respectively, T is the temperature, k_B is the Boltzmann constant, and $\sigma_{T,h(g)}$ is the standard deviation of the host (guest) triplet density of states, which is assumed to have a Gaussian shape. The second term in the argument of the exponential function describes the effect of triplet relaxation due to diffusion of molecules with (on average) lower triplet energy.

As shown in Fig. 5(b), we extract the values of $P_{T,g}$ from the measured PL intensity decay. We have established in Sec. IV A that for CDBP no deconfinement occurs and can, therefore, use it as a reference with $P_{T,g} = 1$. Relative to the intensity onset in CDBP, we then find $P_{T,g}$ of approximately 0.58 for mCBP, 0.26 for TAZ, and 0.06 for TPBi. The open symbols in Fig. 5(a) show the effective confinement energies $\Delta E_{T,eff}$ that follow from Eq. (1) when assuming $\sigma_{T,h} = \sigma_{T,g}$. Considering that a value for σ_T between 0.04 and 0.06 eV is a typical range for organic materials, the impact of different disorder strengths on $P_{T,g}$ would be at most equivalent to $\Delta E_T \approx 0.04$ eV.³⁸

For comparison, the full symbols show the values of ΔE_T that follow from the photophysical determination from phosphorescence spectra (see Table I). The values are strongly correlated but

FIG. 5. (a) Triplet confinement energy ΔE_T following from photophysical measurements on the individual materials for CzPIME in CDBP, mCBP, TAZ, and TPBi (closed symbols, see Table I). For the three hosts showing deconfinement also the effective triplet confinement energy $\Delta E_{T,eff}$ (open symbols) is shown. $\Delta E_{T,eff}$ follows from Eq. (1), with the guest occupation probability $P_{T,g}$ extracted from the onset intensity of the delayed photoluminescence. The full and dashed lines are guides to the eye, with the same slope and a constant offset of 0.12 eV. (b) Comparison of the measured transient PL (symbols) and KMC simulations thereof (curves), with the $\Delta E_{T,eff}$ indicated in panel (a) and reproducing the experimental value of $P_{T,g}$.

show a relative shift of approximately 0.12 eV. This can be understood from the large width of the TADF phosphorescence spectrum, for which the onset energy is about 0.35 eV larger than the peak energy (see Fig. S3 of the [supplementary material](#)). Due to the large energetic disorder of the intramolecular CT-excitons on the TADF molecules and possibly the presence of multiple strong vibrational modes, no vibronic substructure can be distinguished. The determined emission peak is then redshifted with respect to the 0-0 peak. For comparison, the difference between the first (0-0)

peak and the onset energy of the triplet emission spectrum is only 0.1 eV or even less for typical host materials, also studied at 77 K (see e.g., Ref. 39). Effectively, the energy barrier for deconfinement is thus overestimated when deducing the host and guest triplet energies from the spectral peak positions.

While deconfinement decreases the onset intensity of the delayed emission by a factor $P_{T,g}$, it is at the same time expected to increase the delayed emission lifetime by a factor $1/P_{T,g}$. The longer lifetime increases the probability of non-radiative triplet decay on the host, as well as the probability of quenching at defects or impurities. The PL efficiency is thereby reduced with increasing deconfinement, as is observed experimentally (see Table I). Figure 5(b) shows a comparison between the measured and simulated time-dependent PL intensities, using the KMC simulation tool Bumblebee.²⁵ The simulations are performed as described in Ref. 26 for the fast-diffusion limit, with a small adaptation to include $k_{nr,T,h}$, the non-radiative decay rate on the host: in Eqs. (7)–(10) of that work all factors $P_{T,g}k_T$ (the total loss rate from the triplet state of the TADF emitter) should be replaced by $[P_{T,g}k_T + k_{nr,T,h}(1 - P_{T,g})]$.

With the previously determined photophysical rates of the emitter (see Table II), we find that the simulated PL efficiency for emission from CzPIm in mCBP, TAZ, and TPBi matches the experimental η_{PL} (see Table I) for $k_{nr,T,h} = 2.0, 6.0$, and $1.5 \times 10^4 \text{ s}^{-1}$, respectively. In the case of mCBP, which still shows a very high PL efficiency of 62%, the excitons do not spend enough time on the host to suffer significantly from non-radiative losses. The deconfinement, in this case, results only in a decrease in the PL intensity during the delayed regime.

A clear difference for the simulated time-dependence of the PL is still visible in Fig. 5(b) for $t > 2 \times 10^{-6} \text{ s}$, where the simulations predict an approximately exponential decay. The non-exponential decay observed in the experiment could be explained by deeper exciton-trap sites on the host than are included by the Gaussian distribution of energy levels or distribution of photophysical rates.⁴⁰ For TPBi, the simulation result also deviates from the experiment for short delay times in the prompt regime. Given its small dissociation barrier ($\Delta E_{\text{HOMO}} = -0.04 \text{ eV}$), it is possible that a small degree of dissociation occurs in TPBi, enabled by a relatively large disorder. Such a broadened disorder can be caused by the significant dipole moment of TPBi ($\mu = 7 \pm 3.4 \text{ D}$).⁴¹

We conclude that at room temperature, deconfinement starts to play a role when the triplet confinement energy ΔE_T that is deduced from the peak energy of the emitter spectrum and the 0-0 peak energy of the host spectra is smaller than about 0.25 eV. The effective confinement energy [see Fig. 5(a)], from which the reduction of the delayed emission intensity can be estimated, is approximately 0.12 eV smaller. As has been discussed above, this discrepancy is most likely related to the broad and unresolved nature of the CzPIm emission peak.

C. Dissociation

1. Experimental evidence of dissociation

The emission from CzPIm:host (5 mol.%) thin films with TCTA and TAPC as hosts shows a clear redshift and the PL efficiency is drastically decreased, from a maximum of 65% to 15% (TCTA) and 7% (TAPC), as shown in Table I. Furthermore, a

featureless decrease in the intensity with time rather than distinct prompt and delayed emission regimes are observed [Fig. 4(b)]. These observations indicate that for both systems exciton dissociation is significant. As discussed in Sec. I, we expect that the relevant dissociation process is the transfer of a hole from the emitter to a host molecule so that an intermolecular CT-state is formed. TCTA and TAPC are indeed the two systems for which the activation barrier for dissociation is smallest, as is clear from Figs. 2 and 3. Triplet deconfinement is not expected to play a role, as the confinement energy $\Delta E_T > 0.25 \text{ eV}$ is large in both materials.

Although dissociation depletes the population of guest-excitons, in both TCTA and TAPC the relative remaining PL intensity (i.e., when plotting the normalized signal) in a time window around 10^{-7} s is actually larger than for systems without dissociation. For the TCTA system, the spectrum shows a redshift and a broadening of the emission peak [0.6 eV full width at half maximum, compared to 0.5 eV for the CzSi system, see Fig. 4(a)]. This means that also longer-lived radiative decay from CT-states must contribute to the emission. At present, the relative weight of both contributions cannot be quantified, as the pure CT-state emission spectrum and PL efficiency are not available. For the TAPC system, on the other hand, effectively all emission originates from the respective CT-state. The larger redshift for this system, as compared to that for the TCTA system, is qualitatively consistent with the smaller (less negative) HOMO energy for TAPC, leading to energetically more favorable CT-states.

2. Simulation model

We use a rate-equation model to analyze the fraction of formed CT-states, the contribution of CT emission to the overall spectrum and the resulting PL efficiency, as well as the time-dependence of the intensity decay. The model assumes that the optical excitation, if it occurs on a host molecule, is followed by a very fast exciton transfer to the guest. The exciton population at $t = 0$ then consists entirely of singlets on the TADF emitters. Within the model, the emitter resides at the origin of a simple cubic lattice of host molecules. Even though our work thus neglects the actual structural disorder of the amorphous materials, we find by a comparison with simulation results for an fcc lattice that the sensitivity to the detailed structure is very weak (see Sec. S7 in the supplementary material). The lattice parameter (intermolecular distance) is $a = 1 \text{ nm}$, which is a typical intermolecular distance in the considered systems. The TADF emitter site is labeled $j = 0$ and the surrounding nearest neighbor host sites are labeled $j = 1, \dots, 6$ (NN) and the next-nearest neighbors $j = 7, \dots, 18$ (NNN), etc. An electron-hole pair state after dissociation of an exciton can be in several different configurations: either it is in the NN configuration at a separation of $d = 1 \text{ nm}$, which only then we denominate as a “CT-state.” Or a subsequent hop has occurred after dissociation leading to a separation of $d = \sqrt{2} \text{ nm}$, which is denoted as a NNN-state.

If the third-nearest neighbors are included as well, the number of host sites included in the model becomes $N_{\text{tot}} = 26$. In this case, nearest-neighbor hopping of the dissociated hole up to an electron-hole separation of $d = \sqrt{3} \text{ nm}$ becomes possible. Unless

stated otherwise, a total of $N_{\text{tot}} = 18$ host sites are included in our modeling results.

The nominal activation energy for creating an electron-hole pair with the hole on a host site at a distance d_j is given by

$$E_{A,j,\text{nom}} = \Delta E_{\text{HOMO}} + E_{\text{exc,b}} - \frac{e^2}{4\pi\epsilon_0\epsilon_r d_j}, \quad (2)$$

with $E_{\text{exc,b}}$ being the nominal binding energy of an exciton on a CzPIME molecule. The last term in the expression is the nominal electron-hole pair binding energy, $E_{\text{ch,b},j}$. This energy is assumed to be equal to the Coulomb energy between an electron and a hole at a distance d_j in a medium with relative permittivity ϵ_r , where ϵ_0 is the vacuum permittivity. We neglect the small difference between the singlet and triplet binding energies of the TADF excitons.

With a typical value of $\epsilon_r = 3$, the CT and NNN binding energies are $E_{\text{CT,b}}(1 \text{ nm}) = 0.48 \text{ eV}$ and $E_{\text{NNN,b}}(\sqrt{2} \text{ nm}) = 0.34 \text{ eV}$, respectively.⁴² It is clear from the experiment that at least some of the dissociated states have a radiative decay channel available. We will assume in the model that the CT-states ($d = 1 \text{ nm}$) have a radiative decay rate, but that the farther separated electron-hole pair states ($d > 1 \text{ nm}$) are non-emissive. The observed redshift of the total emission peak with respect to the intrinsic TADF emission peak is then expected to be close to the nominal activation energy for dissociation to a NN-site. In the TAPC host, the spectrum shows a redshift of approximately 0.33 eV [see Fig. 4(a)]. From Eq. (2), with $\Delta E_{\text{HOMO}} = -0.88 \text{ eV}$ and $E_{\text{b,CT}} = 0.48 \text{ eV}$, we can estimate the exciton binding energy $E_{\text{exc,b}}$ for CzPIME to be about 1.0 eV.

To include the important aspect of the energetic disorder in the organic semiconductor, we model the guest and host sites for many random disorder configurations m . The HOMO energy for each site j is then assumed to deviate from the nominal value by $\delta E_{\text{HOMO},mj}$, which is taken from a Gaussian distribution with a width σ . The activation energy between two sites is then given by

$$E_{A,mj} = E_{A,\text{nom}} + \delta E_{\text{HOMO},m0} - \delta E_{\text{HOMO},mj}. \quad (3)$$

For the sake of notational simplicity, we will omit in the following the label m when indicating process rates or exciton densities.

Just as in our earlier OLED material and device simulations, we describe the kinetics of charge transfer, exciton generation, and exciton dissociation using the Miller-Abrahams formalism.^{43–46} Here, we only consider the possibility of hole-transfer between nearest-neighbor sites in the cubic grid. The transfer rate for a hole on an initial site j to a final site k , in the presence of an electron at the TADF emitter ($j = 0$), is then

$$r_{jk} = \nu_{1,h} \exp \left[-\frac{|\Delta E_{A,jk}| + \Delta E_{A,jk}}{2k_B T} \right], \quad (4)$$

with $\nu_{1,h}$ being the hole hopping attempt rate to a NN-site and $\Delta E_{A,jk} \equiv E_{A,k} - E_{A,j}$. The rate for dissociation of a guest-exciton to a CT-state is r_{0k} , and the rate for the reverse process (exciton generation on the TADF guest) is r_{k0} . Consistent with the previous work, a typical value of the hole hopping attempt rate $\nu_{1,h} = 3.3 \times 10^{10} \text{ s}^{-1}$

is chosen.^{46–48} The hole transfer is assumed to be spin-conserving and its rate to be spin-independent.

For the guest-exciton itself as well as all possible electron-hole pair states, we will differentiate between the system being in a singlet or triplet state. This means that we explicitly consider the spin-multiplicity of the electron-hole pair, even after dissociation. Overall, the system can then be in $2(N_{\text{tot}} + 1)$ configurations, where the factor 2 accounts for the singlet and triplet states. The singlet (triplet) states are coupled by spin-mixing, resulting in a spin-flip rate $k_{\text{sf},S(T)}$. The spin-flip rates on the TADF emitter, k_{ISC} and k_{rISC} , are, in general, different due to the presence of a small but still significant singlet-triplet energy gap. For the electron-hole pair states, the singlet-triplet gap can be assumed to be even smaller, resulting in a single spin-independent rate $k_{\text{sf},S} = k_{\text{sf},T} = k_{\text{sf}}$. This is consistent with the findings in Ref. 49 from a CT-state emission study. A more detailed model that includes, e.g., the random size and orientation of the local hyperfine fields around which the electron and hole spins precess, would result in a distribution of spin-flip rates.^{50,51} Here, for the sake of simplicity, spin-transitions in the CT-state are treated as processes with a single value for the rate. The distinction between the three triplet sub-states is thus neglected.

The time-dependence of the normalized density of singlet and triplet states in each configuration, $n_{S,j}$ and $n_{T,j}$, respectively, is obtained by solving the following set of $2(N_{\text{tot}} + 1)$ coupled differential equations:

$$\begin{aligned} \frac{dn_{S(T),j}}{dt} = & -k_{S(T),j}n_{S(T),j} - k_{\text{sf},S(T),j}n_{S(T),j} + k_{\text{sf},T(S),j}n_{T(S),j} \\ & + \sum_{k \in \{\text{NN-set of } j\}} (r_{kj}n_{S(T),k} - r_{jk}n_{S(T),j}), \end{aligned} \quad (5)$$

where the summation includes transfers to and from all (at most six) nearest neighbors of site j that are included in the model, and with

$$\begin{aligned} k_{S(T)} &= k_{\text{r},S(T)} + k_{\text{nr},S(T)} + k_{\text{ISC(rISC)}} \text{ for } j = 0, \\ k_{S(T)} &= k_{\text{r,CT},S(T)} + k_{\text{nr,CT},S(T)} + k_{\text{sf}} \text{ for } j = 1, \dots, 6, \\ k_{S(T)} &= k_{\text{sf}} \text{ for } j = 7, \dots, 18. \end{aligned} \quad (6)$$

As described above, for the PL experiment the initial conditions at $t = 0$ are $n_S = 1$ on the TADF guest site ($j=0$) and zero for all other states.

We extend the two scenarios (see Table II) used to describe the non-radiative decay rates of the emitter to the CT-states. Fits I and II then consider either $k_{\text{nr},T} = k_{\text{nr,CT},T} = 0$ (fit I) or $k_{\text{nr},S} = k_{\text{nr},T}$ with $k_{\text{nr,CT},S} = k_{\text{nr,CT},T}$ (fit II). Independent of the fit scenario, no phosphorescence is assumed so that $k_{\text{r,CT},T} = 0$. We assume that from the non-emissive electron-hole pair states with the hole on farther away host sites ($d > 1 \text{ nm}$) also, no non-radiative recombination can occur. In Subsections IV C 4 and IV C 5, we will determine an estimate of the photophysical rates for the CT-states of CzPIME:TCTA (Table III).

For the simple cubic grid with the six NN-sites and twelve NNN-sites, we find that numerical solutions of Eq. (5) can be obtained using standard solution methods.⁵² An advantage of using this approach is that the accurate solutions are obtained for

TABLE III. Photophysical rates for CT-states in TCTA:CzPIME (5 mol. %) thin films, deduced from a fit to the time-resolved PL intensity and including the PL efficiency (see Sec. IV C 5), for various values of k_{sf} , for $\sigma = 0.1$ (0.2) eV and for fit scenarios I (k_{nr} , CT, $T = 0$) and II (k_{nr} , CT, $T = k_{nr}$, CT, S). The accuracy of the rates is approximately $\pm 20\%$. The fourth column gives the relative contribution of CT-states to the overall emission, $\eta_{CT,rel}$. Bold lettering is used to indicate the set of parameters that we regard as the overall best fit to the PL efficiency and the time-resolved PL intensity, also considering $\eta_{CT,rel}$. The rates of the TADF emitter are given in Table II.

	k_r , CT, S (10^6 s $^{-1}$)	k_{nr} , CT, S (10^6 s $^{-1}$)	$\eta_{CT,rel}$
<i>Fit scenario I</i>			
No spin-flip	0.15 (0.4)	10 (11)	0.08 (0.20)
$k_{sf} = 10^6$ s $^{-1}$	0.5 (0.8)	15 (15)	0.17 (0.27)
$k_{sf} = 10^7$ s $^{-1}$	1.3 (1.2)	22 (22)	0.32 (0.33)
$k_{sf} = 10^8$ s^{-1}	2.6 (2.0)	38 (33)	0.35 (0.33)
$k_{sf} = 10^9$ s $^{-1}$	3.7 (4.1)	43 (55)	0.44 (0.39)
<i>Fit scenario II</i>			
No spin-flip	1.0 (1.4)	7 (12)	0.52 (0.54)
$k_{sf} = 10^7$ s $^{-1}$	1.8 (1.4)	11 (11)	0.47 (0.40)
$k_{sf} = 10^9$ s $^{-1}$	5.1 (4.1)	29 (29)	0.47 (0.38)

all relevant times, all relevant states, and for over more than ten orders of magnitude in the exciton density. Including the next shell of (eight) third-nearest neighbors, at a distance of $\sqrt{3}a$, is found to make the problem mathematically stiff so that even when using very small time steps and a high numerical accuracy not always a solution can be found. However, adding a single third nearest neighbor molecule is often found to be possible. We will show that for the systems that are studied in this work the role of NNN-sites is already quite limited, at least up to delay times of about 10^{-5} s. If needed, kinetic Monte Carlo methods can be used to study dissociation under conditions for which more distant neighbors are involved. The final results shown here are obtained by averaging the solutions of Eq. (5) over typically 1000–10 000 disorder configurations.

3. Fraction of electron-hole pairs

A first view on the critical threshold of ΔE_{HOMO} for which CT-state formation is expected can be obtained simply from the fractions of guest-excitons and electron-hole pair states that are predicted to be formed. Within the model, the time scale within which these fractions reach a near-equilibrium value is very short, of the order $\nu_{1,h}^{-1}$, i.e., in the 10–100 ps range. This is at least two orders of magnitude faster than the relevant photophysical and spin-mixing time scales. For a given disorder configuration, these equilibrium fractions then depend only on the HOMO energies of the TADF and host sites.

Figure 6(a) shows the disorder-averaged total equilibrium fraction of electron-hole pairs, $f_{eh-total}$, for HOMO energy disorder strengths of $\sigma = 0.10, 0.15$, and 0.20 eV. In this case, host sites up to a distance of $d = \sqrt{3}a$ (third-nearest neighbor sites) from the emitter are considered, resulting in $N_{tot} = 26$. $f_{eh-total}$ is then the sum of the fractions in the nearest neighbor configuration (f_{NN} , dashed curves), in the next-nearest neighbor configuration (f_{NNN} , dotted curves), and in the third-nearest neighbor configuration

FIG. 6. (a) Fractions of total electron-hole pairs, $f_{eh-total}$, as well as the fractions in the nearest neighbor (f_{NN}) and next-nearest neighbor (f_{NNN}) configuration, as a function of ΔE_{HOMO} and for various disorder widths σ . Not shown are the third-nearest neighbor configurations. (b) Fraction of CT-states among the photophysically active states (guest-excitons and CT-states). The vertical dashed lines indicate the values of ΔE_{HOMO} for CzPIME in CzSi and TCTA hosts (see Table I). The binding energies used are $E_{exc,b} = 1$ eV and $E_{CT,b} = 0.48$ eV.

(not shown). The activation energy for the hops was obtained from Eqs. (2) and (3), with $E_{exc,b} = 1$ eV and $E_{CT,b} = 0.48$ eV (as estimated above). The figure shows that the ΔE_{HOMO} range within which the crossover from no dissociation to full dissociation takes place broadens with increasing energetic disorder of the HOMO states. Positional variation as a result of a disordered morphology would further broaden the transition. The crossover (when $f_{eh-total} = 0.5$) for a typical disorder energy of $\sigma = 0.1$ eV occurs around $\Delta E_{HOMO} \approx -0.4$ eV. For $\sigma = 0.1$ eV, the role of dissociation to NNN-type pairs is seen to be small, even at the largest HOMO energy offset considered (-0.6 eV). Dissociation to the third-nearest neighbor sites is then insignificant and we conclude that considering host sites up to the next-nearest neighbors in the model will give a good estimation of the electron-hole pair population in the relevant ΔE_{HOMO} range. At higher disorder (0.2 eV), dissociated states on the second- and third-nearest neighbors can become increasingly important. We note that the crossover energy depends linearly on the difference between emitter and CT-state binding energies, $E_{exc,b} - E_{CT,b}$.

Figure 6(b) shows for which ΔE_{HOMO} dissociation starts to become visible in photophysical experiment. The figure gives the disorder-averaged fraction of photophysically active states that is a

CT-state (NN), $f'_{\text{NN}} = f_{\text{NN}}/(f_{\text{emitter}} + f_{\text{NN}})$, again for various disorder energies. For $\Delta E_{\text{HOMO}} = -0.52$ eV, this fraction is seen to be equal to 6/7 and independent of the disorder, because the nominal activation energy for CT-state formation is exactly zero. In the absence of disorder and if $k_{\text{r},\text{S}} = k_{\text{r},\text{CT},\text{S}}$, then f'_{NN} simply gives the relative contribution of CT-state emission to the total PL efficiency, $f_{\text{CT}} = \eta_{\text{PL,CT}}/\eta_{\text{PL}}$. The rates of non-radiative decay on the emitter and CT-states do not affect this, even though they do affect the total PL efficiency as will be shown in Subsection IV C 4. However, for disordered systems, $f_{\text{NN},m}$ and $\eta_{\text{PL},m}$ (with m the disorder configuration) are correlated so that $\eta_{\text{PL,CT}} \neq f'_{\text{NN}} \times \eta_{\text{PL}}$.

4. PL efficiency

As the next step, we analyze the effect of the photophysical rates in the CT-state and of the disorder on the PL efficiency. It seems plausible that the radiative singlet decay from CT-states, $k_{\text{r},\text{CT},\text{S}}$, is of the same order of magnitude as the radiative singlet decay rate $k_{\text{r},\text{S}}$ on the TADF emitter itself, which also has a significant intramolecular CT-character.⁴⁹ Therefore, $k_{\text{r},\text{CT},\text{S}}$ is here taken to be equal to $k_{\text{r},\text{S}}$. From fits to the PL decay in Subsection IV C 5, this is found to be a fair approximation for the CzPIme:TCTA system. It seems also plausible that the non-radiative decay rate of the CT-states is larger than that of the emitter states, in view of the less rigid connection between the separate molecules on which the hole and the electron reside after dissociation. In Fig. 7, we investigate the sensitivity of η_{PL} and f_{CT} to the non-radiative decay rate of the CT-state by varying the ratio $k_{\text{nr},\text{CT}}/k_{\text{nr}}$. Full black and gray curves indicate results without spin-flip of electron-hole pair states and dashed curves indicate results for $k_{\text{sf}} = 10^7 \text{ s}^{-1}$. This is the order-of-magnitude that may be expected for organic molecules, as the hyperfine field B_{hf} that is induced by the hydrogen nuclei is typically 1 mT, leading to a spin precession frequency $f = g\mu_{\text{B}}B_{\text{hf}}/h = 2.8 \times 10^7 \text{ s}^{-1}$.⁵³ Here, g is the electron g -factor, μ_{B} is the Bohr magneton, and h is the Planck constant. The red curves give the fraction of CT-state emission, $f_{\text{CT}} = \eta_{\text{PL,CT}}/\eta_{\text{PL}}$.

Figure 7(a) shows that within fit scenario I (no non-radiative decay of triplets), a decrease in the PL efficiency with lower ΔE_{HOMO} is only expected when the ratio $k_{\text{nr},\text{CT}}/k_{\text{nr}} > 1$. The regime where CT-states affect the PL efficiency is seen to directly depend on this ratio. At small barriers ΔE_{HOMO} , the PL efficiency can be decreased even before the CT-state emission contribution f_{CT} (full thick red curve) becomes significant. It is important to note that the dissociation in this case cannot be detected by a contribution to the overall emission spectrum. As $k_{\text{r},\text{CT},\text{S}} = k_{\text{r},\text{S}}$, this contribution is equal to the quantity f'_{NN} shown in Fig. 6(b) for $\sigma = 0$ eV. Here, the PL efficiency is only determined by the ratio between the singlets on the TADF guest and CT-state singlets, which is time-independent due to the fast hole hopping rate. The overall PL efficiency within fit scenario I is therefore not affected by the spin-flip of electron-hole pair states. However, these spin-flips can strongly affect the time-dependence of the PL intensity, as will be shown in Subsection IV C 5.

Figure 7(b) shows the broadening of the dissociation threshold upon introducing a disorder energy $\sigma = 0.1$ eV. Energetic disorder also causes a shift in the ΔE_{HOMO} threshold for which dissociation negatively impacts η_{PL} , consistent with the trend that was observed

FIG. 7. PL efficiency as a function of ΔE_{HOMO} (black/gray, left axis) and fraction of emission from CT-excited states (red, right axis) with $E_{\text{exc},b} = 1$ eV and $E_{\text{CT},b} = 0.48$ eV. The photophysical rates of the emitter are given in Table II, and for CT-states we take $k_{\text{r},\text{CT},\text{S}} = k_{\text{r},\text{S}}$ while the ratio $k_{\text{nr},\text{CT}}/k_{\text{nr}}$ is varied. The symbols indicate the measured PL efficiency η_{PL} for CzPIme in CzSi and TCTA (left axis). (a) Results for fit scenario I without disorder and no spin-flip and (b) with disorder of $\sigma = 0.1$ eV and no spin-flip. (c) Results for fit scenario II and, for the dashed curves, with a spin-flip rate $k_{\text{sf}} = 10^7 \text{ s}^{-1}$ of the electron-hole pair states.

in Fig. 6. The fraction of CT-state emission is now seen to depend on the non-radiative decay rate of the CT-states.

Figure 7(c) shows that for fit scenario II (equal non-radiative rates from singlet and triplet states) the effect of dissociation on the PL efficiency is more complex. Although η_{PL} decreases with lower ΔE_{HOMO} initially, the curves even show an efficiency increase when ΔE_{HOMO} is below approximately -0.4 eV. That is surprising, given that the non-radiative CT-decay rate is up to a factor $k_{\text{nr},\text{CT}}/k_{\text{nr}} = 100$ larger than that of the TADF emitter. This is due to the dissociation process being much faster than the ISC

on the TADF so that a large fraction of singlet CT-states is formed. These CT-singlets cause the increased efficiency because their non-radiative decay rate is small within this fit scenario and because the spin-flip to the triplet state is slower in the CT-state than on the TADF emitter by ISC. For that reason, fit scenario II also shows a dependency of the PL efficiency on the spin-flip rate of CT-states, shown by the dashed lines in Fig. 7(c). For weakly dissociated systems, the effect on η_{PL} is positive, as the singlet density actually becomes larger. However, for very negative ΔE_{HOMO} , dissociation once more reduces η_{PL} regardless of spin-flip because the rate for forming a guest-exciton again from the CT-state becomes very small. We note that for strongly negative ΔE_{HOMO} values full dissociation to a free electron and hole and subsequent non-geminate recombination will become possible, which is not included in the present model. In the absence of energetic disorder, this regime change will occur when ΔE_{HOMO} is close to the $-E_{\text{exc,b}}$, which is here -1 eV.

5. Time-resolved PL intensity

The time-resolved PL intensity can be used to quantify the rates of the various processes that occur upon dissociation. We focus on the CzPIME:TCTA system for which some, but not all, of the guest-excitons undergo dissociation. The starting point of the analysis is the set of photophysical rates on the emitter molecule that are given in Table II for two fit scenarios (I and II). As mentioned in Sec. IV C 2, we extend fit scenario I by assuming that also on the CT-states non-radiative decay occurs only for singlets and we extend fit scenario II by assuming equal non-radiative decay rates for CT-singlets and CT-triplets. Within each scenario, the free parameters are $k_{\text{r,CT,S}}$, one value for the considered non-radiative decay rates, and k_{sf} . We first take fixed values of k_{sf} and determine the CT-decay rates resulting in (i) an overall PL efficiency of $\eta_{\text{PL}} = 0.15$ (the experimental value, see Table I) and (ii) a crossover time $t_{\text{crossover}} = 3 \times 10^7$ s of the simulated PL intensity curve affected by dissociation and the simulated curve without dissociation [which is consistent with the measurement results, see Fig. 4(b)].

It is not *a priori* clear which value of the HOMO energy disorder should be used. An analysis of measurements of hole transport in TCTA films has led to $\sigma = 0.10$ eV.⁵⁴ Such a value is typical for materials that are based on molecules with small or negligible electrostatic dipole moments. Slightly larger values [$\sigma = 0.136$ eV (Ref. 55) and 0.112 eV (Ref. 54)] have been obtained from first principles simulations. One could argue that in a dissociation experiment the strong field gradient due to the remaining charge on the emitter molecule, combined with positional disorder, increases the effective energetic disorder. On the other hand, short-range electrostatic fields from the molecular quadrupole moments make the disorder spatially correlated and effectively weaker with regard to a local process such as CT-state formation. Based on these considerations, we focus on simulation results that have been obtained for $\sigma = 0.1$ eV, even though we will also give results for larger values of σ . We note that an indirect argument that favors the use of a value of $\sigma = 0.1$ eV is that the experiments do not show evidence for CT-state formation when using as a host CzSi, a stable amorphous material with a high glass temperature, and a

relatively small molecular dipole moment.^{31,56,57} From Fig. 6, with a realistic uncertainty of ± 0.1 eV in ΔE_{HOMO} , this finding could not be well explained if σ would be much larger than 0.1 eV.

Table III gives an overview of the best fit results for $\sigma = 0.1$ and 0.2 eV and for various values of k_{sf} . The table shows that the parameters depend only weakly on σ , but show a significant dependence on k_{sf} . The effect of introducing a spin-flip rate is largest for scenario I, within which only singlet states show non-radiative decay. With increasing k_{sf} , the difference between both scenarios becomes smaller. This near-convergence of both fit scenarios for $k_{\text{sf}} \sim 10^9 \text{ s}^{-1}$ is reflected by the similarity of the rates $k_{\text{r,CT,S}}$ and $(k_{\text{nr,CT,S}} + k_{\text{nr,CT,T}})$. The relative contribution of CT-state emission to the time-integrated PL intensity, $\eta_{\text{CT,rel}}$, is then around 45%.

The overall fit quality and the required k_{sf} to best match the experimental time-resolved PL intensity can be judged from Fig. 8. All intensity curves are normalized at $t = 10^{-9}$ s, as the intensity for much shorter times is not experimentally accessible. All panels show a decrease in the simulated PL intensity around 10 ps, when electron-hole pairs are formed. Panels (a) and (b) show how the emission depends on σ and on the inclusion of only NN-sites [panel (a)] or also NNN-sites [panel (b)] in the absence of electron-hole pair spin-flips. In the experimentally accessible time range, up to approximately 3×10^{-5} s, the effects of an increase in the disorder energy or the inclusion of NNN-sites is seen to be relatively weak. Interestingly, the weak but extremely long-lived intensity for $t > 10^{-4}$ s is approximately linear on the double-logarithmic scale used. This long-lived tail is more pronounced with increasing disorder energy. Such a near-linearity can be due to the near-exponential distribution of activation barriers for detrapping of holes from deep NNN sites in the tails of their Gaussian density of states. The observed slope of the intensity curves, which is approximately -1.3 for $\sigma = 0.2$ eV, agrees well with such a distribution of activation barriers (see Sec. S5 of the supplementary material).

For both fit scenarios, the curves in panels (a) and (b) still show a distinct transition from prompt to delayed emission, whereas in the experimental decay these regimes are no longer visible. Instead, the experimental intensity decay from $t = 10^{-7}$ to 10^{-5} s is approximately linear on the double-log scale used.

Panel (c) in Fig. 8 shows that for a system that includes NNN-sites, with fit scenario I and $\sigma = 0.1$ eV, the observed disappearance of the prompt-delayed transition can be understood when introducing spin-flips in the CT-state. For times up to 10^{-5} s, a similarly good agreement can be obtained with fit scenario II (see Sec. S6 of the supplementary material). For low spin-flip rates, the relative emission from CT-states $\eta_{\text{CT,rel}}$ within this scenario is then significantly higher as compared to fit scenario I (see Table III). As discussed in Sec. IV C 4, we regard values of k_{sf} in the range 10^7 – 10^8 s^{-1} , resulting from hyperfine field interactions, as realistic for the materials studied. In that range, fit scenario I shows better agreement of $\eta_{\text{CT,rel}}$ with the CT-state emission observed experimentally for the TCTA system.

For large delay times however, the simulation results with $k_{\text{sf}} \approx 10^8 \text{ s}^{-1}$ that are shown in panel (c) still do not agree well with the experiment. The experimental data [Fig. 4(b)] suggest that at 10^{-4} s the normalized PL intensity is still 10^{-5} – 10^{-4} , whereas the simulation results show a decrease in an intensity below 10^{-6} .

FIG. 8. Simulated transient PL intensity for $\Delta E_{\text{HOMO}} = -0.47$ eV (CzPIMe:TCTA). All panels include as a reference (black dotted curve) the modeled decay for CzPIMe without CT-state formation (CzPIMe:CzSi; see Fig. S4 in the [supplementary material](#)) as well as the experimental reference data for CzPIMe:TCTA (dashed green). (a) Simulations without spin-flip including only NN host sites for fit scenarios I and II and for $\sigma = 0.10, 0.15$, and 0.20 eV. (b) Same as (a), but with inclusion of NNN host sites, which are also included in (c) and (d). (c) Simulations for fit scenario I, with realistic $\sigma = 0.1$ eV, showing the impact of varying k_{sf} . (d) Simulations for fit scenarios I and II at large disorder $\sigma = 0.2$ eV, and comparing $k_{\text{sf}} = 0$ with a very fast spin-flip rate $k_{\text{sf}} = 10^9 \text{ s}^{-1}$. For clarity, all scenario I results in this panel are offset by two orders of magnitude.

This observation indicates that a small fraction of the sites forms hole traps with longer release times than included by the Gaussian HOMO distribution. As suggested already by the disorder-dependent results in panel (b), the experimental results could in principle be explained by assuming a large disorder energy, combined with a strong spin-flip. Indeed, the simulation results in panel (d), for $\sigma = 0.2$ eV and $k_{\text{sf}} = 10^9 \text{ s}^{-1}$, yield a PL intensity that is similar to the measured data. However, as argued in Subsections IV C 3 and IV C 4, we regard such a strong HOMO disorder as less likely. Alternatively, the effect could be due to extrinsic trap states. We find indeed that adding a single third-nearest neighbor site as a strong hole trap, i.e., with a 0.5 eV more shallow HOMO energy, can cause the observed extension of the linear (on a log-scale) decay curves without significantly affecting the PL intensity up to 10^{-5} s (see Sec. S7 of the [supplementary material](#)).

For entirely dissociating systems (effectively all guest-excitations dissociate to at least a NN-site), the PL efficiency η_{PL} is equal to $\eta_{\text{PL,CT}} = k_{\text{r,CT,S}} / (k_{\text{r,CT,S}} + k_{\text{nr,CT,S}})$ and independent of ΔE_{HOMO} . From the best fit deduced for the TCTA system (bold in [Table III](#)), the efficiency for CT-state emission is then $\eta_{\text{PL,CT}} = 0.068$. Interestingly, this value is very similar to the experimental PL

efficiency of the TAPC system (0.07, see [Table I](#)) for which the emission is almost entirely from CT-states.

In summary, we have estimated the photophysical properties of the TCTA:CzPIMe CT-state, as shown in [Table III](#), from fitting and simulations of the transient PL intensity. The lack of distinct prompt and delayed regime is a result of the spin-flip in the CT-states in combination with the HOMO energy disorder, leading to a wide-spread distribution of properties for the CT-states formed on different guest sites. The model reproduces the modified decay dynamics and PL efficiency well. Nonetheless, for both the TADF guest and the CT-states, the analysis does not reveal where the non-radiative loss occurs (from singlet or triplet states, using, for example, fit scenario I or II).

6. Time-integrated CT-state emission spectrum

The model that has been developed above can also be used to calculate the contribution to the emission spectrum from CT-states that would be expected in the absence of vibronic broadening. Within this approximation, the shift of the emission energy from a CT-state on a specific CzPIMe–host molecule pair, with respect to the emission energy from CzPIMe, is equal to the pair-specific

activation energy for CT-state formation [Eq. (3)]. Figure 9(a) shows for various nominal values of ΔE_{HOMO} the CT-state emission spectrum that would then be expected for the CzPIME:TCTA system, using the best fit parameters obtained previously (bold in Table III). The emission peaks have a full width at half maximum that increases from about 0.1 to 0.2 eV in the ΔE_{HOMO} range studied and show a distinct redshift for ΔE_{HOMO} below -0.4 eV, when dissociation becomes significant. Shown in the inset of Fig. 9(b) is the integral of these CT-state emission spectra, which gives the CT-state contribution to the PL efficiency, $\eta_{\text{PL,CT}}$. Figure 9(b) gives the average shift of the emission energy with respect to that of the TADF emitter. For cases with strong dissociation, the redshift approaches the nominal value of the activation energy for CT-state formation that is given by Eq. (2) (short-dashed line). The results for $\Delta E_{\text{HOMO}} \leq -0.6$ eV are connected using a long-dashed curve, instead of a full curve, in order to emphasize that in this part of the parameter range the model might not be fully correct as a result of full dissociation, followed by non-geminate pair recombination. Including that effect, which will also depend on the emitter concentration, is beyond the scope of this study. The figure shows that for the CzPIME:TCTA system, with $\Delta E_{\text{HOMO}} \approx -0.47$ eV, a redshift of the CT contribution of approximately -0.10 eV is expected. For the assumed set of parameters, CT emission then contributes about 35% of the total intensity (see Table III). Considering the limitations of the modeling approach and experimental uncertainties, the calculated redshift of the CT-spectrum may be regarded as being in good agreement with the observed redshift of -0.13 eV (see Table I) of the total spectrum.

7. Time-resolved contribution of CT-state emission

For a given disorder configuration, the relative CT-state contribution to the emission spectrum increases as a result of dissociation until a time $t \sim \nu_{1,h}^{-1} \sim 3 \times 10^{-11}$ s and becomes then constant. The value of $\nu_{1,h}$, the hole hopping attempt rate to the nearest-neighbor, is much larger than the rates of all other processes. This means that the established ratio between all singlet densities n_{S_j} remains unchanged by the following processes. However, we find that for an ensemble of emitters with different disorder configurations the relative CT-state contribution to the emission spectrum is even for $t > \nu_{1,h}^{-1}$ not constant. Figure 9(c) shows the time-dependence of the fraction of CT-state emission for various values of ΔE_{HOMO} . The main effects are the development of a peak at $t \sim 10^{-7}$ s and a broad minimum around $t \sim 10^{-5}$ – 10^{-6} s. The time range of high CT-emission around 10^{-7} s agrees very well with the relatively increased intensity in the experimental PL decay for TCTA and TAPC [see Fig. 4(b)]. For $t > 10^{-4}$ s, where the emission intensity is very small and determined by particularly deep host trap sites, no statistically accurate results could be obtained.

The time-dependence of the CT-state contribution can be understood as follows. After the very fast formation of a quasi-equilibrium between TADF-singlet and CT-state singlets, at $t \sim 3 \times 10^{-11}$ s, the spin-flip of CT-states at $t \sim k_{\text{sf}}^{-1} = 10^{-8}$ s is the next process that affects the population of the various excitonic states. The number of singlet CT-states is reduced more strongly

FIG. 9. Properties of the CT-state emission, obtained from simulations using fit scenario I with $\sigma = 0.10$ eV and $k_{\text{sf}} = 10^8 \text{ s}^{-1}$, and using the emitter and CT-state photophysical rates that are given in Tables II and III. (a) Spectral intensity for various values of ΔE_{HOMO} . The relative emission energy $\Delta h\nu$ is defined with respect to the emission peak of the TADF emitter. (b) Disorder-averaged change of the CT-emission peak energy in dependence of ΔE_{HOMO} . The short-dashed line gives the result that is obtained in the absence of energetic disorder. The results for $-\Delta E_{\text{HOMO}} \geq 0.6$ eV are indicated using a long-dashed curve, in order to emphasize limitations of the model in that part of the parameter range (see the main text). The inset shows the ΔE_{HOMO} dependence of $\eta_{\text{PL,CT}}$, the CT contribution to the overall PL efficiency. (c) Time-dependent fraction of CT-state emission. The dashed curve gives the result for $\Delta E_{\text{HOMO}} = -0.47$ eV with $k_{\text{sf}} = 0$ (but otherwise equal rates).

for disorder configurations with energetically favorable CT-states. The configuration-averaged fraction of CT-state singlets therefore decreases, resulting also in a decrease in the fraction of CT-state emission. As may be seen from Fig. 9(c), this decrease is soon followed by an increase caused by ISC on the TADF emitter. It occurs around $t \sim k_{\text{ISC}}^{-1} \sim 3 \times 10^{-8}$ s and strongly reduces the population of singlets for disorder configurations in which they are still located on the TADF emitter. With this depopulation of singlets on the guest, the ensemble-averaged contribution of CT-state singlets to the overall singlet population increases once more. Just like ISC has effectively more impact in disorder configurations with a relatively large exciton population on the emitter, the same holds for rISC. Already at $t \sim 3 \times 10^{-7}$ s, rISC leads to a significant repopulation of singlets on the TADF emitter and once more a decrease in the fraction of CT-state emission. Much later, at $t \sim (1 - 3) \times 10^{-5}$ s, disorder configurations with holes trapped in non-emissive NNN-sites return to the CT-state so that the CT-state emission fraction finally again increases.

These simulation results suggest that measurements of the time-dependent emission spectra for systems with partial CT-state emission, such as the TCTA:CzPIMe system, could be used to more sensitively probe the mechanism of the dissociation and to more accurately quantify its rate parameters.

V. SUMMARY AND CONCLUSIONS

The aim of this study has been to develop refined criteria for the selection of suitable host materials for donor-acceptor type TADF emitters. For that purpose, we have studied the emission spectrum and the time-resolved emission intensity of eight thin films with 5 mol. % of the TADF emitter CzPIMe embedded in various host materials. From an analysis of the experimental data and using a comprehensive simulation model, we have identified and quantified the relevant material parameters of the host and guest materials. The key observation on which the analysis is based is that among the eight systems studied three types of host-guest systems could be distinguished depending on the electronic and excitonic energy level structures of the two materials.

First, for three of the host materials used, emission exclusively from the TADF guest emitter and with identical prompt and delayed emission intensities were observed. Furthermore, for two of those hosts, the PL efficiencies were among the highest measured (61% and 65%), while for the third no determination was possible. We could conclude that these three host materials allow for no detrimental interactions with the guest. The time-resolved PL experiments in these hosts were then used to accurately determine the emitter's intrinsic photophysical properties.

Second, we observed exciton deconfinement for three host-guest systems, i.e., the transfer of a triplet from the TADF emitter to the host material. We find that this process is well-suppressed when the confinement barrier ΔE_T is larger than 0.25 eV, defined as the difference between the peak energy for emission from the TADF guest and the energy of the 0-0 peak in the triplet spectrum of the host. The reduction of the delayed fluorescence intensity upon deconfinement was found to be consistent with the analysis given in Ref. 26 for the "fast diffusion limit." Deconfinement is here described by the reduced probability $P_{T,g}$ that the triplets reside on

a TADF emitter molecule [Eq. (1)]. The $P_{T,g}$ values determined in this study correspond to effective values $\Delta E_{T,\text{eff}}$ that are 0.12 eV smaller than ΔE_T for all three hosts. We attribute the discrepancy to the underestimation of the TADF emitter's triplet energy, resulting from taking the peak value of the very broad emission spectrum instead of a value more closer to the onset of the spectrum.

Third, we observed for TCTA and TAPC as host materials that the excitons on the TADF emitter can dissociate and form intermolecular charge-transfer states. For both of those hosts, the PL efficiency is strongly decreased, the emission spectrum shows a redshift, and the time-resolved intensity shows no discernible prompt and delayed components. Instead, the intensity follows an approximately algebraic time-dependence ($\propto 1/t^\alpha$ with $\alpha \approx 1.2$). As both TCTA and TAPC have a shallower HOMO energy than CzPIMe, we interpret these observations as a result of hopping transfer of a hole, leading to the formation of (partially) emissive electron-hole pair states. The activation energy for this process is equal to the guest-host HOMO energy difference, $\Delta E_{\text{HOMO}} = E_{\text{HOMO,g}} - E_{\text{HOMO,h}}$, which was determined using UPS measurements of the neat films, plus the difference $E_{\text{exc,b}} - E_{\text{CT,b}}$ of the guest-exciton and CT-state binding energies. From the large measured redshift for the TAPC system, we deduce that the exciton binding for CzPIMe is approximately 1.0 eV. This value might be considered surprisingly large, as the exciton binding energy is expected to be relatively small for the typical TADF donor-acceptor type molecules such as CzPIMe. From a combined photoemission and inverse photoemission study, the singlet exciton binding energy for various fluorescent emitters was indeed found to be larger (in the range 0.9–1.3 eV) than the value of ≈ 0.63 eV that was found in the same study for the prototypical TADF emitter 4CzIPN [1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene].⁵⁸ The large value for CzPIMe is a result of the relatively small size of the molecule, with a distance of only about 0.3–0.4 nm between the electron donating and electron accepting carbazole and phthalimide parts. However, not being a dedicated study of the binding energy, the analysis from which $E_{\text{exc,b}}$ has been extracted contains various uncertainties, such as the values of ΔE_{HOMO} and $E_{\text{CT,b}}$ [see Eq. (3)], as well as the hole hopping attempt rate $\nu_{1,h}$. We estimate the resulting combined uncertainty to be in the range of $\pm(0.2 - 0.3)$ eV.

In order to analyze the experimental results, an extended rate-equation model was developed that includes the effects of the energetic disorder of HOMO states, host-guest transfer of holes, radiative and non-radiative decay of the CT-states, spin-flip of CT-states, and possible further dissociation. It was extensively applied to the specific case of the CzPIMe:TCTA system. For this system, TADF and CT-state emission contribute with a ratio of approximately 2:1 to the overall emission. A PL efficiency and time-resolved intensity that is consistent with the observations is obtained when assuming a disorder energy of 0.1 eV. We find a radiative decay rate for CT-state emission similar to that of the TADF-emitter and a non-radiative decay rate that is about one order of magnitude larger. The comparison with the experiment provides evidence for significant spin-flip between singlet and triplet CT-states, with a rate k_{sf} of the order 10^7 – 10^8 s⁻¹. The uncertainty in this rate is in part due to the finding that the modeling is not sensitive to the precise nature (occurring from singlets or

triplets) of the non-radiative decay of the photophysically active states.

We have shown that for the specific set of host–guest systems studied, dissociation to intermolecular CT-states is effectively suppressed when $\Delta E_{\text{HOMO}} \approx -0.2$ eV. More generally, we expect that for systems with the same energetic disorder and similar CT-state properties suppressing dissociation requires that $\Delta E_{\text{HOMO}} \approx -E_{\text{exc,b}} + 0.8$ eV. As shown in this work, the binding energy $E_{\text{exc,b}}$ of the excitons on the TADF emitter follows readily from the observed redshift in a strongly dissociating host. Prerequisites for the determination in this way are that the emission occurs entirely from CT-states and that $E_{\text{CT,b}}$ is well-estimated by assuming a dielectrically screened nearest neighbor Coulomb interaction energy. $E_{\text{exc,b}}$ is expected to depend on the distance between the donor and acceptor type groups on the TADF emitter. This implies that smaller TADF emitters have less strict requirements regarding hole confinement to the host's HOMO level, which can have significant consequences for the transport of holes through the EML in the full OLED stack. It will be of interest to verify this generalized criterion by carrying out systematic studies of the type that has been presented here, for TADF emitters with a varying $E_{\text{exc,b}}$. Another interesting extension of this study would be a temperature variation, though it is well beyond the scope of the present work given the experimental and modeling requirements and challenges. Such a study could further elucidate to what extent the developed models provide a proper description of the thermally activated triplet deconfinement and dissociation processes.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for the UPS measurement data for the emitter in Sec. S1 and for the host materials in Sec. S2. Section S3 contains the emitter's phosphorescence spectrum and Sec. S4 shows the fitting of the emitter's transient PL decay that leads to the extracted rates shown in [Table II](#) of the main paper. Section S5 analyzes the effect of a broad distribution of activation barriers for hole detrapping. Section S6 shows the effect of the spin-flip rate on the transient PL decay within fit scenario II. Section S7 demonstrates the effect of a single third-nearest neighbor site on the transient PL decay.

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DATA AVAILABILITY

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

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