

# Thermally Activated Delayed Fluorescence in Polymer–Small-Molecule Exciplex Blends for Solution-Processed Organic Light-Emitting Diodes

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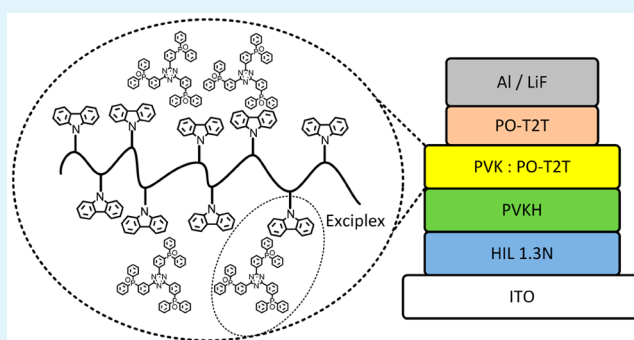
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## Supporting Information

**ABSTRACT:** The photophysics of an exciplex state formed between a small molecule and a polymer is investigated in this work. The results obtained with this blend show the strong potential of polymer–small-molecule blends for triplet harvesting in organic light-emitting diodes (OLEDs) via thermally activated delayed fluorescence. The exciplex formed between poly(*N*-vinylcarbazole) (PVK) and 2,4,6-tris[3-(diphenylphosphinyl)phenyl]-1,3,5-triazine (PO-T2T) shows yellow-green emission and is applied in solution-processed OLEDs. The excellent film-forming properties in this blend allow easy spin coating and potential use in other solution-processing techniques, such as slot die coating. In this work, we critically address the reverse intersystem crossing mechanism in the presented exciplex system, including the role of local triplet states. Moreover, we bring a clear physical meaning to the decay components of the exciplex emission, including the decay occurring in a power-law fashion that is often ignored in the literature.

**KEYWORDS:** OLED, TADF, exciplex, polymer, photophysics



## INTRODUCTION

Since the fabrication of the first organic light-emitting diodes (OLEDs) by Tang and VanSlyke,<sup>1</sup> OLEDs have shown strong potential for application in lighting and display technologies.<sup>2,3</sup> The use of vacuum thermal evaporation (VTE)<sup>4–6</sup> is currently the method of choice in the fabrication of the most efficient OLEDs that are already in use in smart phones and television displays. However, because of the large material consumption, cost, and the need for spacious high-vacuum chambers and complicated shadow masks, VTE is likely to be used only in high-end applications, where high quality is favored over the production cost. Therefore, the objective of fabricating OLEDs at low cost directly from solution in large area remains alive. Techniques such as roll-to-roll, slot die, or inkjet printing can reduce material usage and costs associated with the long-standing aim of printing luminaires and displays. However, these techniques require preferably well-soluble materials with high molecular weight. Burroughes and co-authors<sup>7,8</sup> made the first polymer-based OLEDs. Since then, many polymers and dendrimers have exhibited their usefulness for application in OLEDs, and the development of such emitters is still ongoing.<sup>9–14</sup>

From the historical point of view, OLEDs started to be fabricated with purely fluorescent organic compounds, which

were then superseded by more-efficient organic metal-complex emitters.<sup>15</sup> This breakthrough opened a pathway to increase exciton harvesting efficiency from 25% up to 100%. Nowadays, the metal complex emitters are being challenged by novel thermally activated delayed fluorescent (TADF) molecules and polymers, which also allow for 100% triplet harvesting.<sup>16,17</sup> Remarkably, without using platinum or iridium. Several TADF emitters have been reported in the literature, showing triplet-harvesting yields close to 100%,<sup>15,18</sup> including D-A3 molecular structures (one star-shaped donor with three acceptors attached to it) with multiple singlet–triplet state pairs.<sup>19</sup> TADF materials have also been used as hosts for phosphorescent metal complexes.<sup>20</sup> Moreover, by using purely hydrocarbon hosts, Cui et al.<sup>21</sup> achieved nearly 100% exciton harvesting for both phosphorescent and TADF dopants. However, still no exciplex-based device realizing 100% exciton harvesting has been shown.<sup>22</sup>

Small-molecule TADF materials have been widely investigated to understand their photophysical and physicochemical properties; however, polymer-based and dendrimer materials,

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which are more suitable for cost-efficient solution-processing methods, have been relatively neglected and solution-processed TADF devices remain elusive.

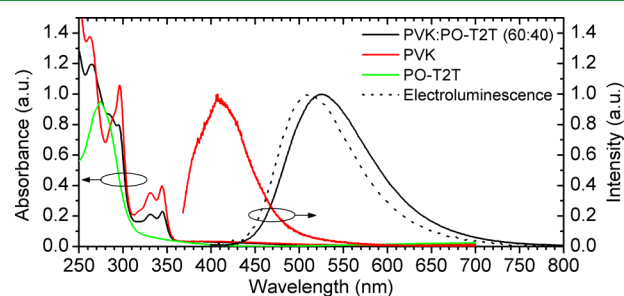
An interesting concept is to use commercially available or easy-to-synthesize donor and acceptor materials, which are not TADF on their own, but may form TADF exciplexes.<sup>23–30</sup> Such exciplex systems may show TADF properties, providing that proper energy alignment between the exciplex intermolecular charge-transfer state (<sup>1</sup>CT) and the local triplet state (<sup>3</sup>LE) is met.<sup>5,26</sup> In particular, we intend to find blends with high photoluminescence yield (PLQY) and good TADF properties. This requires solving a tradeoff between the energy alignment of the singlet CT and the local triplet <sup>3</sup>LE states, to maximize reverse intersystem crossing (RISC), and suppressing the efficiency of the nonradiative decay rates.

Exciplex systems have been investigated mainly between small-molecule-based emitters, which are suitable for vacuum thermal evaporation or similar techniques, but not for solution-processing methods, since, typically, the fabrication of high-quality films with small molecules is very challenging, using solution processing methods. In contrast, TADF polymer-based exciplex systems allow for efficient triplet harvesting and are suitable for inkjet and slot die printing. In this work, we explore a polymer–small-molecule blend to obtain efficient TADF, using the formation of intermolecular exciplex states between the polymer PVK, acting as the electron donor, and the small molecules PO-T2T, acting as the electron acceptor unit (see Figure 1). This blend can be easily processed from solution and, to the best of our knowledge, is the first attempt to produce a polymer–small-molecule exciplex, for the purpose

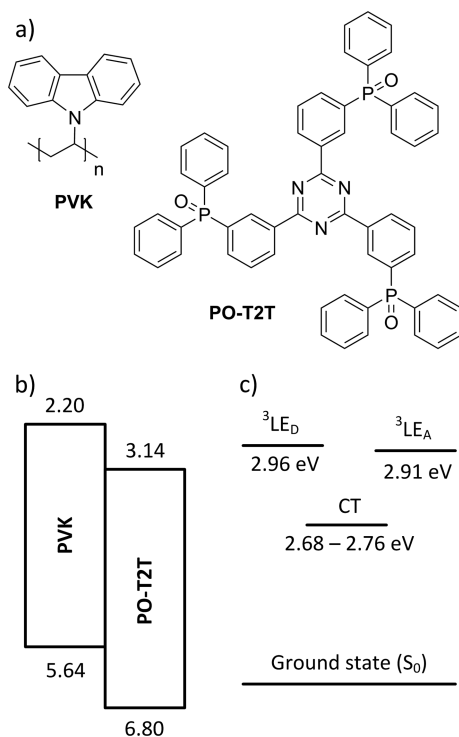
of strong TADF emission. Because of the prominent film-forming properties of poly(*N*-vinylcarbazole),<sup>31,32</sup> the blend can potentially be used in inkjet or slot-die printing. 2,4,6-Tris[3-(diphenylphosphinyl)phenyl]-1,3,5-triazine (PO-T2T),<sup>25</sup> which is used as an acceptor, shows excellent solubility in toluene, which helps in the formation of high-quality films.

## RESULTS AND DISCUSSION

Excited-state intermolecular charge transfer (CT) complexes (exciplexes) are formed between electron donor and acceptor species only in the excited state.<sup>33–35</sup> Therefore, no ground-state interaction between the donor and acceptor species exist, and, the absorption spectrum of the blend is the sum of the donor's and acceptor's absorption (see Figure 2).



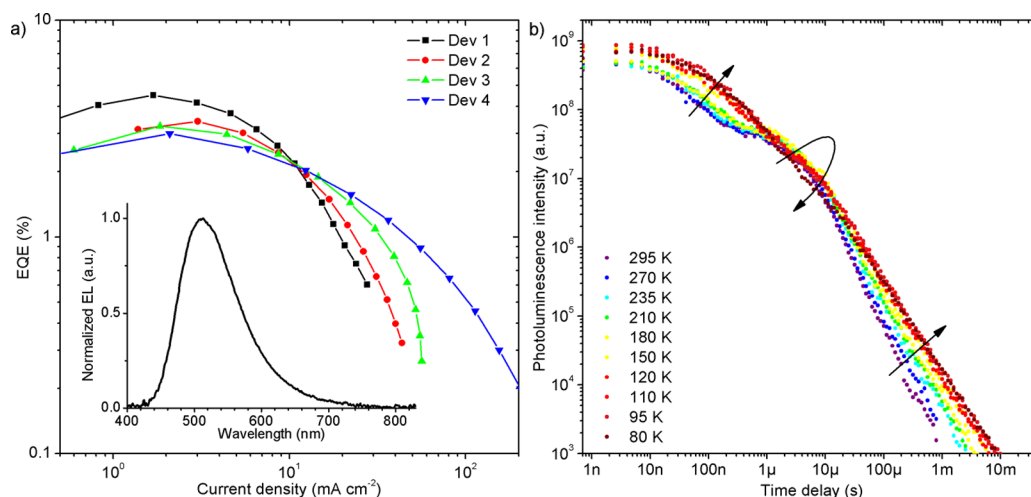
**Figure 2.** Absorption and photoluminescence (PL) spectra of donor, acceptor and the blend compared with device electroluminescence (EL) (for PL,  $\lambda_{\text{ex}} = 355$  nm). Note that PO-T2T shows no clearly detectable PL in neat film. Previous works show a very weak PL from PO-T2T film.<sup>39</sup>



**Figure 1.** (a) Structures of donor (PVK) and acceptor (PO-T2T) materials used in this work; (b) schematic diagram of electronic energy levels of the donor and acceptor molecules in ground state; (c) excited-state energy diagram of the exciplex blend. <sup>3</sup>LE<sub>D</sub> and <sup>3</sup>LE<sub>A</sub> denote the triplet states localized on the donor and the acceptor, respectively.

The energy of the exciplex intermolecular CT state is roughly a function of the donor's ionization potential (IP<sub>D</sub>) and the acceptor's electron affinity (EA<sub>A</sub>).<sup>34,35</sup> These are usually identified as the HOMO<sub>D</sub> and LUMO<sub>A</sub> energies, respectively.<sup>36,37</sup> The formation of the exciplex leads to an emission spectrum that is significantly red-shifted, relative to donor and acceptor emissions. In the case of poly(*N*-vinylcarbazole) (PVK), IP<sub>D</sub> = 5.64 eV,<sup>38</sup> and PO-T2T, EA<sub>A</sub> = 3.14 eV,<sup>25</sup> this can clearly be seen in Figure 2. PVK shows weak blue emission, and the PO-T2T emission is too weak to be recorded. However, the blend of these two materials shows strong green CT photoluminescence (PL) ( $\Phi_{\text{PL}} = 0.12 \pm 0.02$  in air and  $\Phi_{\text{PL}} = 0.20 \pm 0.03$  in nitrogen).

Since the PVK:PO-T2T blend possesses prominent luminescent properties and shows TADF, it is therefore an ideal candidate for use in OLEDs as the emitting layer. These two materials are highly soluble in toluene. In particular, when low-molecular-weight PVK (PVKH) is used in the blend, high-molecular-weight PVK (PVKH) can then be used as the hole-transport/electron-blocking layer, which helps to improve device performance.<sup>40,41</sup> PO-T2T is also used as an electron-transport/hole-blocking layer. However, electron transport and injection layers and cathode are evaporated, but all other layers are solution-processed. This leads to the following device structure: ITO | HIL 1.3N (45 nm) | PVKH (10 nm) | PVK:PO-T2T (60:40) (*x* nm) | PO-T2T (50 nm) | LiF (0.8 nm) | Al (100 nm), where *x* = 0 (Dev 4), 6 ± 1 (Dev 3), 16 ± 2 (Dev 2), and 27 ± 2 nm (Dev 1) (see Figure 3a, Figures S5–S11 in the Supporting Information, and Table 1).



**Figure 3.** (a) EQE versus current density characteristics of OLEDs; inset shows EL spectrum of Dev 4. (b) Photoluminescence decay of PVK:PO-T2T exciplex at various temperatures ( $\lambda_{\text{ex}} = 355$  nm).

**Table 1. Characteristics of OLED Devices**

device	$x^a$ (nm)	turn-on voltage, $V_{\text{ON}}$ , at 1 cd m <sup>-2</sup> (V)	maximum EQE / EQE at 10 mA cm <sup>-2</sup> (%)	maximum current efficiency / current efficiency at 10 mA cm <sup>-2</sup> (cd A <sup>-1</sup> )
Dev 1	27 ± 2	4.9	4.5/2.3	13.3/6.8
Dev 2	16 ± 2	4.4	3.4/2.2	10.0/6.5
Dev 3	6 ± 1	3.7	3.3/2.2	9.8/6.5
Dev 4	0	2.6	3.0/2.1	9.3/6.3

<sup>a</sup>Device structure: ITO | HIL 1.3N (45 nm) | PVKH (10 nm) | PVK:PO-T2T (60:40) ( $x$  nm) | PO-T2T (50 nm) | LiF (0.8 nm) | Al (100 nm).

A PVK:PO-T2T ratio of 60:40 was used to allow for sufficient hole and electron transport properties of the emissive layer and also to reduce the recombination at the PVKH interface. It is later presented that a variation in the PVK:PO-T2T ratio does not affect the CT state, and only a large disproportion between donor and acceptor (such as 1:99) can cause a significant local state emission (see Figures S1 and S2 in the Supporting Information).

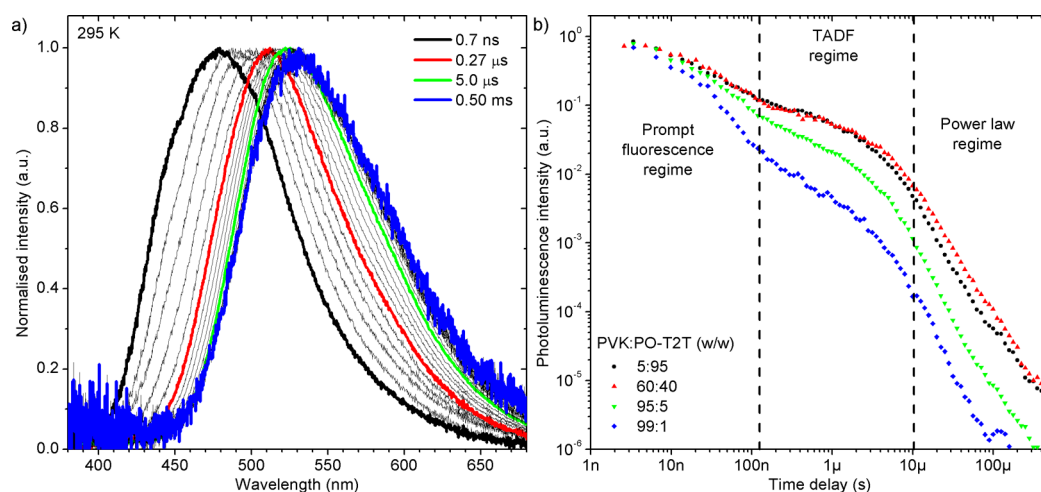
Variation of the emissive layer thickness allows for control of the current density and turn-on voltage ( $V_{\text{ON}}$ ). The device with the thickest emissive layer (Dev 1) shows the highest EQE (4.5%). In contrast, the lowest turn-on voltage ( $V_{\text{ON}} = 2.6$  V) and the highest maximum brightness is observed in Dev 4, which uses no blend donor–acceptor emissive layer ( $x = 0$  nm). In this case, the recombination occurs at the PVKH | PO-T2T interface. Interestingly, the electroluminescence (EL) spectrum is not affected by the emissive layer thickness or by the molecular weight of the donor material, and all devices (Dev 1–Dev 4), show similar EL spectrum at maximum brightness (see Figure S5 in the Supporting Information). Generally speaking, thin devices provide better charge conductivity; thus, the observed current densities increase significantly from Dev 1 to Dev 4. This is caused by the relatively low conductivity of the PVK:PO-T2T blend (more likely due to the low hole mobility of PVK itself); thus, a thin layer provides less resistance. As a result, devices with thicker PVK:PO-T2T layer show lower brightness than devices with thinner or no PVK:PO-T2T layer (Dev 4). Reducing the thickness slightly affects the charge balance, decreasing the maximum EQE of Dev 2–Dev 4, relative to Dev 1, but in

contrast, the change in current density is much more pronounced. The variation in the optical turn-on voltage between Dev 1–Dev 4 is again caused by the low conductivity of PVK. Thinner PVK:PO-T2T layer provides larger current density at lower driving voltage, thus the 1 cd m<sup>-2</sup> brightness threshold is achieved at lower  $V_{\text{ON}}$ .

The EL spectrum is slightly blue-shifted, relative to the PL (Figure 2). Further examination of the EL spectra under various driving voltages (Figures S6–S9 in the Supporting Information) shows that a small blue-shift in the spectrum (affecting both the peak and the onset) upon increasing the voltage can be observed. This is more clearly seen in Dev 4 than in the other cases, while in the thickest device (Dev 1), this can hardly be observed. This effect is very likely to be caused by the electric field, changing the CT energy of the emissive species, as reported previously by Al-Attar et al.<sup>42</sup> While the blue-shift caused by the electric field shows a maximum amplitude of ~7 nm (at the peak), the shift between EL and PL is ~13 nm (at the peak). This observation shows that the electric field may be an important, but not the only, cause of the shift between PL and EL. This also suggests that the PL and EL may show different contributions of the time-resolved emissive components, i.e., the contribution of the most red-shifted power law emission in PL may not be present in the EL.

Less device efficiency roll-off is observed on devices with thin or no PVK:PO-T2T layer (Dev 3 and Dev 4) than in those with thicker EML (Dev 1 and Dev 2) (see Figure 3a). The actual mechanism causing the roll-off on device efficiency is still not clear and may be caused by a superposition of many different processes. Therefore, this is a very complex issue.<sup>43</sup> However, on the basis of some of our observations, possible major mechanisms can be proposed to explain the behavior of Dev 1–Dev 4. First, the thicker EML allows more space for the recombination zone to spread out, which is more likely to move upon changing the applied voltage. This may lead to unfavorable charge balance at higher driving voltage, leading to a decrease in EQE. In the thin devices (Dev 3 and Dev 4), the recombination zone is either tightly localized between the PVKH and PO-T2T layers or is basically related to the PVKH/PO-T2T interface and is not likely to shift easily. As a consequence, there is little or no change of the charge balance in those devices at higher applied voltage. Second, triplet–





**Figure 4.** (a) Time-resolved PL spectra of PVK:PO-T2T (60:40) exciplex blend at 295 K. (b) Photoluminescence decay of PVK:PO-T2T blends at 295 K with various donor–acceptor ratio ( $\lambda_{\text{ex}} = 355$  nm).

triplet annihilation (TTA) and charge trapping phenomena are less likely to appear in thinner layers or at the interface. Thus, TTA-related roll-off is more pronounced in Dev 1 and Dev 2 than in Dev 3 and Dev 4.

The EQE value of 4.5% achieved in Dev 1 is a result of triplet harvesting by the TADF mechanism. Considering the  $\Phi_{\text{PL}} = 0.20 \pm 0.03$ , the EQE achieved in Dev 1 is close to the physical limit (see section S4 in the Supporting Information). Therefore, if TADF was not involved in the EL produced in this OLED, the EQE would only reach  $\sim 1\%$ – $1.5\%$ . This assuming an outcoupling factor of  $\sim 0.2$ – $0.3$ . Although the EQE remains below the values reported for vacuum-deposited small-molecule TADF emitters, these proof-of-concept devices already open a pathway for future research, which may lead to more efficient solution-processed devices. PVK has been found to possess many trapping sites, which may, in fact, quench some of the emissive excitons;<sup>44</sup> therefore, new exciplex-forming polymers must be developed to possibly improve the EQE.

Time-resolved photophysical analysis of the PVK:PO-T2T luminescence reveals that the exciplex emission shows two exponential components, followed by a power-law emission (see Figure 3b, as well as Figure S12 in the Supporting Information). The first exponential component is the short-lived prompt fluorescence ( $\tau = 32 \pm 1$  ns), and the second exponential decay is the long-lived delayed fluorescence ( $\tau = 2.9 \pm 0.2$   $\mu$ s). The power-law emission is likely originated from nongeminate charge recombination of free carriers produced in the blend, as described in previous work.<sup>45</sup> This is discussed later in the text and in the Supporting Information. Interestingly, the PL of the exciplex is significantly affected by nonradiative decay. This is visible as an increase of prompt and delayed fluorescence emissions, between 295 K and 180 K, with decreasing temperature. However, in the temperature range from 180 K to 150 K, the delayed fluorescence intensity switches away from the trend observed at higher temperatures and starts to decrease with temperature, as it is normally expected for a thermally activated process. This behavior is related to the suppression of the RISC rate, with decreasing available thermal energy. The temperature dependence in this region down to 80 K is very small, suggesting a negligible (close to zero) singlet–triplet gap in the exciplex.

The exciplex time-resolved emission, collected using a gated iCCD camera, reveals the entire complexity of the excited-state dynamics in this system. The exciplex emission gradually red-shifts over time (Figure 4a), showing a rapid change between 0.7 ns and 270 ns, for both the onset and emission peak. This is an intermediate region between prompt and delayed fluorescence, and it shows the most significant spectral changes, which can be related to the relaxation of the exciplex geometry, i.e., due to changes in the distance between the donor and acceptor molecules, which affects CT character through the Coulombic factor. Further changes in the spectrum occur between 270 ns and 5  $\mu$ s and are probably due to the emission appearing from multiple CT states, with slightly different energies. It appears that different CT states are formed between PO-T2T molecules and various polymer sites, as a function of their distance. This effect induces the energy distribution associated with the exciplex state that involves PVK and PO-T2T molecules located at different distances, as well as PVK states that involve different numbers of *N*-vinylcarbazole repeating units. Although a variation on the exciplex energy clearly exists, a dominant state is present as the TADF decay component can easily be fitted using a single exponential equation. This occurs probably because the RISC rate is slower than the energy relaxation of the CT state in the exciplex, i.e., the RISC occurs predominately from the most stable CT states. Therefore, we use the emission spectra from this region to estimate the relaxed CT energy, which is further discussed in the context of TADF. Note that the emission intensity in this time range shows a linear dependence with excitation power, which is indicative of the TADF mechanism (see Figure S4 in the Supporting Information).

The power-law decay that is observed from 5  $\mu$ s to 10  $\mu$ s onward follows the TADF emission (see Figure 3b, as well as Figure S12). Within this region, no significant changes in the emission spectrum are observed; however, the emission is different from the spectra observed during the TADF exponential regime. Therefore, the origin of the power-law delayed emission is clearly different from that of the TADF regime. We believe this power-law emission decay is not created by direct upconversion of triplet states, but rather from nongeminate charge recombination. This has been observed previously in exciplex blends<sup>38,45</sup> and is caused by the dissociation of some of the CT states formed in the exciplex,

which, upon dissociation, migrate through the blend as free charge carriers, until recombination later occurs. Polymer-based exciplex blends may be even more likely to undergo this process than small molecules as the charges (i.e., holes or electrons) may be transported not only by hopping between the molecules (or between polymer chains), but also along the polymer backbone (via hopping between grafted carbazole units, not through the backbone itself). This power-law emission intensifies at lower temperatures, since the longer CT state lifetime under these conditions promotes charge dissociation. Moreover, the free carriers migrate slower and are less prone to nonradiative deactivation processes.

Interestingly, the local triplet levels of the molecules forming the exciplex: PVK ( $T_1 = 2.96$  eV)<sup>44</sup> and PO-T2T ( $T_1 = 2.91$  eV; see Figure S14 in the Supporting Information) are clearly above the CT energy, determined from the delayed fluorescence spectra in Figure 4a ( $^1\text{CT} = 2.68\text{--}2.76$  eV). In contrast with intramolecular CT states, where a good energy alignment between CT and local triplets has been proposed to be key for efficient triplet harvesting,<sup>5,46–49</sup> in the case of intermolecular exciplexes, we find that an energy alignment where the  $^3\text{LE}$  is above or isoenergetic with the CT facilitates efficient TADF emission.<sup>23,25,27,50–54</sup> Recently, it has been suggested that the  $^3\text{LE}$  state plays a crucial role in the reverse intersystem crossing (RISC) mechanism when the  $^1\text{CT}$  lies above it or is isoenergetic with it.<sup>5,17,26,47,55–57</sup> It appears that the RISC mechanism in small TADF molecules clearly involves the mixing of local and CT triplet states ( $^3\text{LE}$  and  $^3\text{CT}$ ), as it has been observed from the temperature-dependent studies of TADF in various intramolecular exciplexes. However, the situation in intermolecular exciplexes may be different. Here, the  $^3\text{LE}$  state clearly lies above the  $^1\text{CT}$  state by 0.15–0.23 eV, and it is less evident for the local triplets to be involved in the RISC process, at least in the way that is suggested by the current theory models. Especially, the  $^3\text{CT} \rightarrow ^3\text{LE} \rightarrow ^1\text{CT}$  involving an endothermic  $^3\text{CT} \rightarrow ^3\text{LE}$  upconversion to a higher local triplet state appears to be questionable in this case. The exciplex described here shows an energy difference of >0.15 eV between the  $^1\text{CT}$  and the  $^3\text{LE}$  of PO-T2T. This would clearly quench the TADF at 80 K if this gap was relevant. Instead, TADF is only slowed at this temperature, but can still be easily observed. Moreover, a vast majority of recently studied efficient TADF intermolecular exciplexes show that the CT states are located well below the triplets of the donor and acceptor moieties.<sup>22,25,39</sup> Therefore, we conclude that, for intermolecular exciplex systems, the most common energy layout is the one where the  $^3\text{LE}$  state lies above the  $^1\text{CT}$ , and where the involvement of the local triplet state in the RISC is unlikely. Previous studies suggested that the ISC and RISC processes due to spin–orbit coupling between pure singlet and triplet charge transfer states is forbidden.<sup>5,47,56,57</sup> However, in the case of intermolecular exciplexes, where negligible energy gap between  $^1\text{CT}$  and  $^3\text{CT}$  is achieved, hyperfine interactions might become predominant and originate RISC with negligible loss, as no low energy triplet exists below the CT states.

To further understand the properties of the investigated exciplex blend various D–A ratios have been studied (see Figure 4b, as well as Figures S1 and S2). Remarkably, the ratio between donor–acceptor does not affect exciplex emission at all. All blends show the same CT emission spectrum and lifetime. This is different from the previously observed dependence of the CT energy upon changing the donor–

acceptor ratio.<sup>23,27</sup> However, if extremely large excess of PVK is used, this leads to inefficient local emission of the donor, which reduces the contribution of efficient exciplex emission. A similar situation may occur in devices, leading to recombination on the PVK, thus reducing EQE. This property shows that using various, but not extreme, PVK:PO-T2T ratios to optimize recombination in the device is a prominent strategy.

It was also found that, when using PVKH as the electron blocking layer (EBL), the optimal donor–acceptor ratio is close to a 60:40 mass ratio. However, if an additional EBL cannot be used because of technological limitations, then this ratio may be changed without any effect on photophysics (i.e., by increasing amount of PVK to reduce current leakage).

## CONCLUSIONS

A novel highly luminescent TADF exciplex has been demonstrated, analyzed, and applied in solution-processed devices. The work presents a novel concept of using polymer-based exciplex blends to obtain efficient TADF emission with good solution-processing properties, and potential use in practical low-cost applications. This opens a new pathway in the use of intermolecular exciplexes in commercial applications, but also paves the way for new fundamental research, regarding the RISC mechanism in these systems. We believe PVK:PO-T2T blend is only a first and not fully optimized example of such polymer-based exciplexes, and further development of new polymers as donors or acceptors will occur as natural consequence of the concept described in this work. We also show that a variation in the donor–acceptor ratio does not affect the CT state properties at all. However, extreme ratios such as 99:1 may lead to a decrease in exciplex formation efficiency and thereby cause strong local fluorescence. We also addressed the role of the local triplet states in the RISC mechanism in exciplexes, where the CT state lies below the  $^3\text{LE}$ . Our results show that local triplet states are likely not playing a dominant role in the reverse intersystem crossing mechanism in these blends and probably the RISC mechanism involves significant hyperfine interactions.

## ASSOCIATED CONTENT

### Supporting Information

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Experimental methods, supplementary figures, and discussions (PDF)

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### Notes

The authors declare no competing financial interest.

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