Mixed-Host Systems with a Simple Device Structure for Efficient Solution-Processed Organic Light-Emitting Diodes of a Red-Orange TADF Emitter

Manish Kumar†‡ and Luiz Pereira§†

†Department of Physics and i3N—Institute for Nanostructures, Nanomodulation and Nanofabrication, University of Aveiro, 3810-193 Aveiro, Portugal
‡CeNTI—Centre for Nanotechnologies and Smart Materials, R. Fernando Mesquita, 2785, 4760-034 Vila Nova de Famalicão, Portugal

ABSTRACT: Charge balance, concentration quenching, and exciton confinement are the most important factors for realizing the use of thermally activated delayed fluorescence (TADF) emitters for organic light-emitting diodes. Red-orange organic light-emitting diodes of a TADF emitter 2-[4 (diphenylamino)phenyl]-10,10-dioxide-9H-thioxanthen-9-one (TXO-TPA) have been reported by doping in a mixed p-type host system of poly(N-vinylcarbazole) (PVK) and 1,3-bis(N-carbazolyl)benzene (mCP) via solution-processed. We have demonstrated the peak external quantum efficiency of 9.75%, maximum current efficiency of 19.36 cd/A, and power efficiency of 12.17 lm/W along with a CIE coordinate of (0.45, 0.51). The devices were compared with different doping concentrations of TXO-TPA, and a comparative investigation on the effect of the thickness electron transport layer was studied. The results clearly indicated that this solution-processed TXO-TPA device structure is a promising strategy to develop highly efficient but simple OLED structures.

1. INTRODUCTION

Thermally activated delayed fluorescence (TADF) was first rationalized by Perrin in 1929,1 but since the first successfully application to organic emitters by Adachi and co-workers in 2012 on a simple molecular design principle, their use in fabrication high-efficient organic light-emitting diodes (OLEDs) has been a topic of interest among the researchers throughout the world.2 In the past few years, various results have been reported on molecular design, computational simulation, synthesis, and their use in fabrication of OLEDs via solution and thermally vacuum processed using TADF emitters.3–11 Pure organic molecules exhibiting TADF process are usually considered as the third-generation electroluminescence (EL) materials for OLEDs.2,5,6

Different from conventional organic molecules, TADF process is as one of the most attractive methods for harvesting both singlet (S₁) and triplet (T₁) populations in metal-free organic materials because they can achieve a theoretical maximum internal quantum efficiency (IQE) up to 100%.2,4,7,11–14 In TADF materials, the triplet excitons (T₁) are readily upconverted in a singlet state (S₁) by virtue of the reverse intersystem crossing (rISC) because of their near a zero S₁−T₁ splitting (ΔE₀).2,7,13 Therefore, all S₁ population emit light via a prompt (direct emission, spin-allowed) or delayed fluorescence (via rISC repopulation of S₁ state) achieving that high IQE values.4,13 Despite the significant progress that has been made in recent years, TADF technology still has significant challenges to achieve a full understanding of the TADF mechanism and improve the stability of the devices containing TADF materials and improve the radiative recombination in the emissive layer (EML).16 In addition, an efficient and reliable simple OLED structure for real market applications in the large-area 2D diffuse emitter lighting is the need of the current technology.

For TADF emitters, the main objective of the researchers is to confine all singlet and triplet excitons generated by charge recombination in EML.17 Because of the high probability of emission quenching, TADF-based emitters are usually employed in an OLED as a doping (guest) into a suitable matrix (host) that should also allow an efficient energy transfer to the emitter via Förster and/or Dexter process. This requires specific characteristics of host materials, for which a high T₁ (>3.0 eV) to prevent exciton quenching.15 Second, the host should ensure the complete charge transfer (CT) to the TADF.3,5,7,11,15,18 Third, feasible charge carrier-transporting abilities are needed to increase the recombination within the emitting layer.19 Therefore, in TADF-based OLEDs, the host material plays a more vital role in the triplet harvesting effect, compared to phosphorescent OLEDs.20,21 Most TADF molecules are donor–acceptor (D–A) or donor–acceptor–donor (D–A–D)-type moieties, which give the bipolar characteristics to a TADF molecule.7,11 Several approaches have been studied to improve the host/guest concept in TADF emitters, although the best framework can be emitter-
dependent. Recently, was proposed that, if in a host/guest system based on a TADF dopant, the charge transport is via hole transport in the TADF molecule and simultaneously the electron transport is via the host molecule, therefore the highest occupied molecular orbital (HOMO) levels of the host should be deeper than HOMO levels of TADF. However, in all the host molecules, this is not the ideal case because of p-type or n-type or bipolar characteristics of them, which can change the entire characteristics of the device. Moreover, if the (as typical) the electrical mobility of electrons and holes is clearly distinct, the recombination region inside the EML will have a profile in terms of location/width almost not ideal (i.e., near electrodes and/or wide) with further decrease of efficiency and device lifetime/stability. Another issue of TADF emitters is the well-known influence of the host polarity in the emission not only shifting the main emission but, particularly important, conditioning the efficiency. Other side, ensuring high triplet of host and charge balance to boost efficient energy transfer and reduce self-aggregation of TADF emitters, can adopt a mixed host system. Recently, this concept has been used for fabrication of blue and white OLEDs and a mixed bipolar host for highly efficient OLEDs, exhibiting an external quantum efficiency (EQE) of 18.86%. Nevertheless, all of these solutions, although important in the OLED design structure, need to be adapted to the particular emitter. Without doubt, the host concept is almost the main issue currently addressed in the TADF emitters.

Following these concepts, we investigated OLEDs based in a red-orange TADF (TXO-TPA) with the mixed host of p-type matrix of PVK:mCP, where the TADF is the D–A-type moiety. Our main idea is to obtain, in a simple as the possible device structure, figures of merit that should be compatible for the major usual applications.

To date, many red-orange TADF emitters are reported for their use in various applications such as bioimaging, sensors, telecommunications, night vision, and so forth. At present, in the red-orange emitter (in some complex device structures), EQE of nearly 30% is being recently reported, but compared with the blue and green TADF emitters reported earlier, red TADF emitters are clearly underexplored by virtue of their nature of nonradiative transition process and concentration quenching effect induced by a strong donor–acceptor structure. Nevertheless, in high-efficient reported OLEDs, the final device structure was very complex, sometimes with more than five organic layers that are a technological constraint for practical applications. Therefore, decreasing the red OLED structure complexity, but keeping a useful efficiency, should be one of the fundamental keys for the larger production and applications. This recognized as one of the most problems in such red-orange emitters when attempts to reduce device complexity are made. Additionally, the development of a TADF-based OLED in a simple process requires a selection of suitable host and charge transporting materials. Most of these choices relies in the organic layer thickness optimization (depending on the electrical carriers mobility and final device resistance) and the doping concentrations of the TADF to capitalize the potential of TADF by achieving good recombination. To extract the best performance from the TADF-based EML, it is necessary to ensure the balance charge carriers and exciton confinement in it. A balanced charge carrier and recombination zone in TADF-based OLEDs are very sensitive to the organic layer thickness and mobility of carriers in the EML, which should be improved for better device characteristics enhancement. In this framework, the properties of electron transport layer

![Figure 1](https://example.com/figure1.png)
Figure 2. AFM Image of PVK:mCP:TXO-TPA 50 nm thin film in CB for different wt % of TXO-TPA; (a) 5, (b) 8, and (c) 10 wt %.

(ETL) are also crucial for the better charge transport and recombination zone confinement in the device.32

Although the best electrical figures of merit for any organic layer can be achieved using controlled thermal evaporation methods, this technique suffers of several limitation to improve the host properties. Therefore, solution process fabrication of OLEDs appears as very interesting technique because of the higher degree of physical modulation of the electrical properties. Moreover, it is an extremely rapidly evolving technology for both the display and lighting industry.7,33 The choice of fabrication process had driven the research in OLEDs with an aim to maximize the use of materials. Using a vacuum thermal evaporation process, the method involves a more complex device structure for efficient charge carrier transport and charge carrier balance, which consequences a high cost for large area fabrication.7,34,35 Solution process methods, such as spin-coating, roll-to-roll process, and screen printing, can be adopted low-cost large-area fabrication.36,37 At present, an EQE of 31% in solution-processed OLEDs is reported but the device composed of double hole-transport layer with cross-linkable polymers and had a much complex multilayer device structure.7 Although interesting, the structure complexity is too high for large-area applications but shows the concept. On other side, some recent works on both solution and thermally processed TADF OLEDs summarized recent advancements on such processes but they fail to deliver effective charge-transport properties and recombination profile inside EML.7,10,13,38 In solution process technology, the effect of the thickness of EML and ETL is underestimated and not much explored.

In this study, we develop a simple structured OLED with a mixed host consisting of a polymer PVK and a high triplet (2.9 eV) p-type mCP for the red-orange TXO-TPA OLED, in a conventional p–n two-layer structure. This structure exhibits a maximum EQE of 9.75%. This emitter exhibits a high photoluminescence (PL) quantum yield of 83% in 5 wt % TXO-TPA:mCP thin film. This TADF was first reported by Wang et al. in 2014, with an EQE of 18.5% in a thermally vacuum-deposited device28 although no attempt to build a less complex structure based on a solution-processed EML was reported. However, in thermally vacuum-deposited OLEDs, the device structure was complex and so it is worthy to consider its solution-processed counterpart with a relatively simple device structure, in which, although a decrease in the maximum EQE, it is possible to keep the efficiencies in a useful and practical range. Therefore, in the present work, we focused in low complexity of the fabricated device structure, easy to control the fabrication parameters including the control of the doping with a well-balanced device in terms of the overall figure of merits, and the formation of the recombination region near EML/ETL interface. The OLEDs were fabricated with different doping concentrations of TADF, that is, 5, 8, and 10 wt % and different ETL layer thicknesses. These variations on device performance will be discussed, allowing a better understanding of the host/guest concept for efficient balanced TADF-based OLEDs.

2. RESULTS AND DISCUSSION

2.1. Photophysical Characterization and Film Morphology. Figure 1a,b shows the molecular structures of the materials and the energy level diagram. The TXO-TPA UV–vis absorption and PL spectra are shown in Figure 1c,d. Figure 1c shows the absorption spectra of TXO-TPA in solid-state and toluene solution. The absorption spectra of D–A molecule show a major peak at 420 nm which is assigned to CT absorption mainly associated with electron transport from the TPA moiety to TXO moiety, and additional peaks at 350, 300, and 250 nm clearly reflect the sum of TXO and TPA moieties. The emission spectra have a maximum at 590 nm in toluene and are red-shifted to 650 nm in the thin film as previously observed28 and may because of aggregation-induced emission (AIE). The absolute fluorescence quantum yield (Φf) is 40%. However, in nonpolar rigid media Zeonex, this red-orange emitter showed blue-shifted emission at 500 nm, which can be explained by an excited state with a strong 1π−π* character. Such a rigid chromic effect suggests a strong intramolecular CT character 1CT of emissive state (Figure 1d). TXO-TPA has T1 = 2.46 eV excited states with the lower energy gap between S1 and T1 (ΔEET = 0.09 eV). Earlier, PVK has been used as a host material because of its high triplet (T1 = 3.0 eV) energies,40,41 but the low hole and electron mobilities (10−4 cm2 V−1 s−1) and high triplet–triplet annihilation effect does not make it a suitable host for TADF.42 Thus, a blended system of PVK:mCP was chosen for EML, where the high hole mobility (10−4 cm2 V−1 s−1) and a high triplet of mCP (together also the high T1 level of PVK) enable the mixed p-type host system for TADF doping and use in OLEDs. The HOMO and lowest unoccupied molecular orbital (LUMO) levels of TXO-TPA are 5.4 and 3.5 eV, respectively, as previously determined in ref 28. Therefore, the HOMO level of mCP is much deeper than TXO-TPA (6.1 eV), whereas the LUMO level of mCP is 2.4 eV is relatively near the LUMO of TmPyPb (2.7 eV). It is anticipated that a wider band gap and a deeper HOMO of host materials are considered best for better carrier confinements, balance the electron transport, and control of the exciton formation mechanism.45,46

As previously assumed,31 it is consistent to consider that the HOMO level of the active layer should correspond to the deeper HOMO level of the p-type material, and the LUMO level should be considered the highest of the active layer (in...
this case and for both situations, the mCP). With these assumptions, we expect a hole-blocking barrier at the EML/ TmPyPB interface. To estimate the electrical carrier mobility, Liu et al.\textsuperscript{47} demonstrated a power dependence on the concentration of the individual materials in the matrix and consider that an electrical carrier in the matrix has the mobility that can be given by $\mu_{\text{max}} = \mu^C_1 \times \mu^C_2 \times \ldots \times \mu^C_m$, where 1, 2, ..., $m$ corresponds to the different materials, and $C$ is their individual concentration in the host/guest matrix, where $C_1 + C_2 + \ldots + C_m = 1$. The expression is valid for both electrons and holes.

To compare the surface morphology and effect of TADF doping on thin-film formation, spin-coated thin films of PVK:mCP with 5, 8, and 10 wt % TXO-TPA were prepared in chlorobenzene (CB) of 50 nm thickness on the ITO substrate. The importance of such morphology is the relationship with device optic-electrical characteristics as it is known that intrinsic defects arising from low structural molecular conformation give rise to electrically active energy levels that can act as traps for electrical carriers, changing, in a noticeable way, the electrical mobility and exciton recombination profile and density. Figure 2 shows the atomic force microscopy (AFM) images of films for 5, 8, and 10 wt % in CB. The root-mean-square roughness was 0.40, 0.32, and 1.02 nm. The uniformity of films obtained using CB as a solvent is clearly high. No noticeable aggregations were observed in thin films of EML.

2.2. Carrier-Transport Properties. As previously mentioned, the electrical properties of the host are determinant for the OLED behavior. Among all, electrical mobility can be critical. In order to evaluate the carrier-transporting and charge balance properties, hole-only and electron-only devices with EML only, were fabricated. For hole-only devices, a structure of ITO/PEDOT:PSS (40 nm)/EML (50 nm)/PEDOT:PSS (40 nm)/Al (100 nm) was used, and for the electron-only device, the structure was ITO/LiF (2 nm)/EML (50 nm)/LiF (2 nm)/Al (100 nm). Figure 3 shows the $I$–$V$ characteristics of all the wt % devices for both hole- and electron-only devices. The electrical mobility for majority carrier in each kind of device can be estimated by the $I$–$V$ behavior under the Mott–Gurney model.\textsuperscript{29} In this model, $I = A_\text{eff} \varepsilon \mu_{\text{eff}} \frac{V^2}{d}$, where $A$, $\varepsilon$, $d$, and $\mu_{\text{eff}}$ are the OLED active area, electrical permittivity (assuming as usual that the relative electrical permittivity for organic semiconductors is around 3), the film thickness, and the effective mobility (Poole–Frenkel mobility affected by the density of traps), respectively.

In this space charge current limit (SCLC) model, we can extract the electrical mobility where the applied voltage range follows the Mott–Gurney model. For relatively low applied voltage ($\sim$4 V) and for n-type device (electrons), we found $\mu_e \approx 1.58 \times 10^{-7}$, $9.63 \times 10^{-7}$, and $1.23 \times 10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$ for TADF concentration of 5, 8, and 10 wt %, respectively, whereas for hole mobility, we have $\mu_h \approx 4.43 \times 10^{-4}$, $4.12 \times 10^{-4}$, and $3.79 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, for the same TADF concentration, respectively. These values are in line, with some deviations but in the same order of magnitude, with the expected from the mixed electrical mobility as previously explained. Increasing applied voltage, the mobilities tend to increase (Poole–Frenkel mobility dependence with electrical field) but in a short voltage range, the changes are not noticeable. Under high-applied voltages, Mott–Gurney models are no longer applied (deep traps). We should note that whereas $\mu_e$ increases with TADF concentration, the opposite occurs for $\mu_h$. Moreover, the relative low $\mu_e$ in the active layer is almost dependent on the low $\mu_e$ of PVK. Increasing mCP concentration, should improve the electron mobility in EML but the film becomes very inhomogeneous. A compromise was obtained.

2.3. Device Characteristics. All the molecules PVK, mCP, and TXO-TPA have good solubility in CB. The deposition parameters were optimized to maximize device performance. Here, TmPyPB was used as the electron-transport material because of its high electron mobility of $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ and a high triplet of 2.8 eV.\textsuperscript{48} Figure 4 shows the current density–voltage–luminescence, EL spectrum, and efficiencies (current efficiency $\eta_i$, power efficiency $\eta_p$, and EQE) results obtained for device structure ITO/PEDOT:PSS (40 nm)/EML (40 nm)/TmPyPb (30 nm)/LiF (1 nm)/Al (100 nm).

The turn-on voltage ($V_{\text{ON}}$) of the devices was 6 V for 5 wt % OLED and 5 V for the 8 and 10 wt % OLEDs. In the first observation, the lower $V_{\text{ON}}$ can be ascribed to a simultaneous effect of electrical carrier mobility and organic thickness layers that will promote high density of excitons at low electrical field although not optimized as the low efficiencies show. The device with all wt % of TXO-TPA exhibited a low EQE in the range of 3–5.5%. The maximum $\eta_i$ was 6.60 cd/A and $\eta_p$ was 3.46 lm/W for 5 wt %. The device emits a red-orange EL peak with 554 nm, which is independent of the driving voltage, corresponding to the emission of TXO-TPA emitter. Another peak at 625 was also observed because of AIE of TXO-TPA as previously explained.\textsuperscript{28} An additional weak peak around 400 was observed and is attributed to the emission from PVK. The intensity of this PVK emission is less than 2% of the integrated intensity from the EL spectra. No significant change in the CIE coordinates was observed because of the PVK emission. Moreover, the emission tends to decrease upon increasing the doping concentration of the TADF. Although, from the energy level diagram, we do not expect the presence of any PVK emission, and this is unusual because of the interactions in the host/guest between the emitter and PVK during the process of energy transfer that should occurs. The Commission Internationale de L’Eclairage (CIE) coordinates were (0.44, 0.51). The results are summarized in Table 1.

In the EL spectra of all the devices, a redshift was observed upon increasing the TADF concentration that is usual.\textsuperscript{49} At a
lower thickness of TmPyPb (30 nm), the efficiency is low and this ascribed to the asymmetric hole/electron density profile and, thus the recombination zone moves toward the anode interface with further decreasing of the recombination probability.

When the thickness of the ETL was increased to 40 and 50 nm, the device characteristics were improved by almost two-three folds. The $V_{ON}$ was identical to the device with 30 nm ETL. Also, there was no further change in CIE coordinates observed in all the devices. In a simple explanation, $V_{ON}$ depends on the transition from ohmic to space charge region that, by turn, depends on the carrier densities and electrical mobility. Considering that our host/guest EML still being equal in all device structures, only small changes in $V_{ON}$ are expected (in the layer thickness range probed). Therefore, we should focus more in the electrical carrier/exciton profiles in EML. The device with 40 nm ETL exhibited improved EQE of 3.67, 5.71, and 5.80% for 5, 8, and 10 wt % doping (Figure 5). The results are summarized in Table 2. The CIE color coordinates are around (0.45, 0.51).

The maximum $\eta_C$ was 11.36 cd/A and $\eta_P$ was 7.13 lm/W for 8 wt %. This improvement in the device is attributed because of the better confinement of the recombination zone upon increasing the ETL thickness, according to the electron carrier mobility, will change the electrical carrier profile. The devices exhibited EL bands peaked at 563, 563, and 574 nm for 5, 8, and 10 wt %, respectively. Similar discussions carried out about EL bands are still valid.

The best results were obtained with the device with an ETL of 50 nm in a structure of ITO/PEDOT:PSS (40 nm)/EML (40 nm)/TmPyPb (50 nm)/LiF (1 nm)/Al (100 nm) (Figure 6). In this device, we obtain an EQE of 6.02, 9.75, and 5.33% for 5, 8, and 10 wt % doping, respectively. The CIE color coordinates do not change significantly, with the average values of (0.45, 0.51). The results are summarized in Table 3. The maximum $\eta_C$ was 19.36 cd/A and $\eta_P$ was 12.17 lm/W and $L_{max}$ of 2200 cd/m² for 8 wt %. As an interesting point, the brightness values were obtained measuring only the normal emission, without using an integrating sphere. The EL spectra maximum were at 561, 561, and 574 nm for 5, 8, and 10 wt % doping (Figure 5).

The devices were deposited from CB
attributed to the leakage of the electrons in EML because of poor charge balance and thus yielded the reduced efficiencies. The luminescence is also poor in the 30 nm device, which exhibited a reduction of the excitons recombination.

Considering PEDOT:PSS as a metal-like polymer, employed to optimize the hole injection at the anode, in a similar way to use LiF dielectric for cathode injection optimization, by reducing the respective potential barriers, we can assume that our device is a "two-layer" structure model. In such simple two-organic layer type structure (EML/ETL), in general, the mobility of the electrons in the ETL is lower than the hole mobility in EML, and for a better exciton formation and confinement, this mobility matching is prerequisite irrespective of the ETL thickness. The electrical mobilities determined under space charge conditions, match this assumption, at least by approximation. Following the previously mentioned empirical model from Liu et al. for mixed electrical mobility of a mixed organic layer, and assuming that the electron mobility of pure mCP is around $10^{-9}$ to $10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$, we expect $\mu_e$ and $\mu_p$ only for the host in the order of $10^{-8}$ and $10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively. Such values are considerably low (near one order of magnitude) than the values calculated

under space charge conditions and far from the condition abovementioned. Nevertheless, although in relatively small concentration, the TXO-TPA emitter strongly influences the overall mobility in EML. Increasing the TADF concentration, $\mu_e$ tends to increase and the opposite happens with $\mu_p$. An optimal framework can be, therefore, obtained. Hence, finding the optimum device thickness for both EML and ETL, according to the charge carrier mobilities, is essential. The results presented in Figure 6 clearly show that a thin EML of 50 nm leads to a stable and efficient device with an EQE of 9.75%. In this way, and considering the overall electrical carriers mobilities previously indicated, we can expect (from the EML mixed mobilities) that an increase on ETL should lead to a more symmetrical and narrow, near EML/ETL interface, and electron/hole density profile in the active layer contributing for a better result. Because of high electron mobility in TmPyPb, and because a potential barrier for holes exists in the EML/ETL, increasing the ETL layer thickness leads to a more electrically balanced device. It is known that, the exciton recombination efficiency is dependent on the width of the recombination region. As thinner will be such region, higher recombination probability can be obtained. Our
results can be explained on base of this model, in the sequence above discussed.

Thus, the proposed device structure provides simultaneously a: (i) facilitated enhanced electron injection into EML and hole accumulation at the ETL/EML interface for better hole−electron charge balance in EML; (ii) block of exciton by p-type mCP with high charge mobilities and triplet level in a simplified structure; (iii) good match of HOMO levels of TXO-TPA (5.4 eV) with anode work function (5.3 eV) that also reduces the hole accumulation at the anode/EML interface for better charge balance in EML, and (iv) optimized thickness of ETL that provides adequate charge balance and exciton confinement in EML, further increase to the overall device performance.

Naturally that the simplified structure used cannot allow a very high EQE but with the best result obtained, the values are clear in the range of practical applications. The main idea to overcome the pronounceable decrease of efficiencies is to achieve an optimized charge profile density in the active layer that can compensate for the aforementioned problem with an increase of radiative transitions because of the symmetrical recombination density profile obtained. In this work, we show that such possibility can be achieved with interesting results.

The very simple device structure (in practice only two organic layer structure) is a surplus for suitable applications, opening, therefore, a field of TADF-based OLEDs that can be further explored.

3. CONCLUSIONS

In summary, we demonstrated a simple, essentially two-layer device structure, for the red-orange TXO-TPA emitter used as a guest in a p-type host matrix deposited by solution-processed. The device was optimized with the thickness of the ETL of 50 nm, in order to achieve the best exciton recombination profile. The red-orange OLED with TXO-TPA exhibits the maximum EQE of 9.75%, $\eta_C$ of 19.36 cd/A, and $\eta_P$ was 12.17 lm/W for 8 wt % of the emitter in the host. The CIE color coordinates of (0.45; 0.51) are practically constant in all devices independently of the emitter concentration and of the applied voltage. These results are the best obtained based on TXO-TPA by solution-processed. This work can in influence the use of the red-orange TADF emitters for large-area display and lighting applications.

Table 3. Summary of Results Obtained for the Device with Structure ITO/PEDOT:PSS (40 nm)/PVK:mCP:TXO-TPA (x wt %) (40 nm)/TmPyPb (50 nm)/LiF (1 nm)/Al (100 nm) Deposited from CB

| wt % | $\eta_C$ (cd/A) | $\eta_P$ (lm/W) | EQE (%) | $L_{max}$ (cd/m²) | EQE at 100 cd/m² | $J_{ON}$ (mA/cm²) | $V_{on}$ (V) |
|------|----------------|----------------|---------|-------------------|-----------------|------------------|-----------|
| 5    | 12.16          | 6.36           | 6.02    | 1634              | 1.70            | $9.13 \times 10^{-3}$ | 6         |
| 8    | 19.36          | 12.17          | 9.75    | 2200              | 2.12            | $4.35 \times 10^{-3}$ | 5         |
| 10   | 10.42          | 6.54           | 5.33    | 1918              | 1.50            | $1.20 \times 10^{-2}$ | 5         |
4. MATERIALS AND EXPERIMENTAL SECTION

4.1. Materials. TXO-TPA, PVK, and mCP were obtained from Lumtec Corp., 1,3,5-Tris(m-pyridin-3-ylphenyl)benzene (TmPyPB), poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS), and LiF were obtained from Ossila Ltd. All solvents were bought from Sigma-Aldrich. The patterned ITO substrates (resistivity of 20 Ω/□) were bought from Ossila Ltd. All organic materials were sublimed before use.

4.2. Device Fabrication. The simple device structure was ITO (100 nm)/PEDOT:PSS (40 nm)/EML (40 nm)/ETL (Y nm)/LiF (1 nm)/Al (100 nm), where Y = 30, 40, and 50 nm. EML was [PVK:mCP]_{(100−a)/a}TXO-TPA	extsubscript{a}, where a was the wt % of the TADF emitter dopant in the host PVK:mCP (0.70:0.30 in wt %). The substrates were first cleaned in an ultrasonic bath containing 2% v/v Hellmanex solution in water and then in acetone and 2-propanol (IPA). After solvent cleaning, the substrates were UV ozone treated for 5 min. The PEDOT:PSS was filtered with a 0.45 μm polyvinylidene difluoride (PVDF) filter. The PEDOT:PSS layer was spin-cast at 2000 rpm and annealed at 120 °C for 15 min. The EML [PVK:mCP]_{(100−a)/a}TXO-TPA	extsubscript{a} layer (CB solvent) was spin-coated at 2000 rpm after being filtered using a 0.1 μm polytetrafluoroethylene filter and dried in the glovebox at 80 °C for 30 min. The ETL of TmPyPB (with different thickness), the LiF (1 nm) dielectric layer, and the Al (100 nm) metal layer were deposited in a vacuum, at pressure <5 mbar, and then in acetone and 2-propanol (IPA). After solvent cleaning, the substrates were UV ozone treated for 5 min. The PEDOT:PSS was filtered with a 0.45 μm polyvinylidene difluoride (PVDF) filter. The PEDOT:PSS layer was spin-cast at 2000 rpm and annealed at 120 °C for 15 min. The EML [PVK:mCP]_{(100−a)/a}TXO-TPA	extsubscript{a} layer (CB solvent) was spin-coated at 2000 rpm after being filtered using a 0.1 μm polytetrafluoroethylene filter and dried in the glovebox at 80 °C for 30 min. The ETL of TmPyPB (with different thickness), the LiF (1 nm) dielectric layer, and the Al (100 nm) metal layer were deposited in a vacuum, at pressure <5 × 10⁻⁶ mbar, and then in acetone and 2-propanol (IPA). The devices were characterized in the ambient atmosphere without any encapsulation. The OLEDs, initially at 100 cd/m², exhibited a total loss of 10% after 5 h, and after 6–7 h, the total loss in luminance was 60%. This behavior is usually found in nonencapsulated devices.

4.3. Optical, Electrical, and Morphological Measurement. The current—voltage—luminance (J−V−L) characteristics were determined using a Keithley source meter 2425 model and a Minolta LS-100 Chromameter. For the EL spectrum measurement, an Ocean Optics USB4000 spectrometer was used with the sensitivity response in the wavelength range 350–950 nm. PL spectra of studied samples in toluene were collected in the steady state using a photoluminescence spectrometer with an Xe-lamp as an excitation source and R-928 photomultiplier detector. The morphological characterizations were obtained by the Park Systems XE7 Atomic force microscope.

AUTHOR INFORMATION

Corresponding Author
*E-mail: luiz@ua.pt.

ORCID

Luiz Pereira: 0000-0001-5482-0715

Author Contributions

Experimental and investigation: M.K., Writing—original draft: M.K., Writing—review & editing: L.P., work coordination: L.P.

Funding

The authors would like to acknowledge the “Excilights”: Donor–Acceptor Light Emitting exciplexes as Materials for Easy-to-Tailor Ultra-efficient OLED lighting Project from the European Union’s Horizon 2020 research and innovation program under the Marie Sklodowska-Curie grant agreement no. 674990 for providing financial support for this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to thank Maria Joao Pereira for helping in Atomic Force Microscopic experiments.

REFERENCES

(1) Perrin, F. La fluorescence des solutions. Ann. Phys. 1929, 10, 169–275.
(2) Zhang, Q.; Li, B.; Huang, S.; Nomura, H.; Tanaka, H.; Adachi, C. Efficient blue organic light-emitting diodes employing thermally activated delayed fluorescence. Nat. Photonics 2014, 8, 326.
(3) Data, P.; Takeda, Y. Recent Advancements in and the Future of Organic Emitters: TADF-and RTP-Active Multifunctional Organic Materials. Chem.—Asian J. 2019, 14, 1613–1656.
(4) Kumar, M.; Ribeiro, M.; Pereira, L. New Generation of High Efficient OLED Using Thermally Activated Delayed Fluorescent Materials. Light-Emitting Diode—An Outlook On the Empirical Features and Its Recent Technological Advancements; IntechOpen: London, 2018; pp 103–126.
(5) Liu, Y.; Li, C.; Ren, Z.; Yan, S.; Bryce, M. R. All-organic thermally activated delayed fluorescence materials for organic light-emitting diodes. Nat. Rev. Mater. 2018, 3, 18020.
(6) Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. Highly efficient organic light-emitting diodes from delayed fluorescence. Nature 2012, 492, 234.
(7) Yang, Z.; Mao, Z.; Xie, Z.; Zhang, Y.; Liu, S.; Zhao, J.; Xu, J.; Chi, Z.; Aldred, M. P. Recent advances in organic thermally activated delayed fluorescence materials. Chem. Soc. Rev. 2017, 46, 915–1016.
(8) Tsai, K.-W.; Hung, M.-K.; Yao, Y.-H.; Chen, S.-A. Solution-Processed Thermally Activated Delayed Fluorescent OLED with High EQE as 31% Using High Triplet Energy Crosslinkable Hole Transport Materials. Adv. Funct. Mater. 2019, 29, 1901025.
(9) Tao, Y.; Yuan, K.; Chen, T.; Xu, P.; Li, H.; Chen, R.; Zheng, C.; Zhang, L.; Huang, W. Thermally activated delayed fluorescence materials towards the breakthrough of organoelectronics. Adv. Mater. 2014, 26, 7931–7958.
(10) Huang, T.; Jiang, W.; Duan, L. Recent progress in solution processable TADF materials for organic light-emitting diodes. J. Mater. Chem. C 2018, 6, 5577–5596.
(11) Wong, M. Y.; Zyssman-Colman, E. Purely organic thermally activated delayed fluorescence materials for organic light-emitting diodes. Adv. Mater. 2017, 29, 1605444.
(12) Jou, J.-H.; Kumar, S.; Agrawal, A.; Li, T.-H.; Sahoo, S. Approaches for fabricating high efficiency organic light emitting diodes. J. Mater. Chem. C 2015, 3, 2974–3002.
(13) Dias, F. B.; Penfold, T. J.; Monkman, A. P. Photophysics of thermally activated delayed fluorescence molecules. Methods Appl. Fluoresc. 2017, 5, 012001.
(14) Yerin, H. Highly efficient OLEDs: Materials Based on Thermally Activated Delayed Fluorescence; Wiley-VCH: Weinheim, 2018.
(15) Im, Y.; Kim, M.; Cho, Y. J.; Seo, J.-A.; Yook, K. S.; Lee, J. Y. Molecular design strategy of organic thermally activated delayed fluorescence emitters. Chem. Mater. 2017, 29, 1946–1963.
(16) Cui, L.-S.; Ruan, S.-B.; Bencheikh, F.; Nagata, R.; Zhang, L.; Inada, K.; Nakanotani, H.; Liao, L.-S.; Adachi, C. Long-lived efficient delayed fluorescence organic light-emitting diodes using n-type hosts. Nat. Commun. 2017, 8, 2250.
(17) Kim, J. H.; Yun, J. H.; Lee, J. Y. Recent Progress of Highly Efficient Red and Near-Infrared Thermally Activated Delayed Fluorescent Emitters. Adv. Opt. Mater. 2018, 6, 1800255.
(18) dos Santos, P. L.; Ward, J. S.; Bryce, M. R.; Monkman, A. P. Using Guest-Host Interactions To Optimize the Efficiency of TADF OLEDs. J. Phys. Chem. Lett. 2016, 7, 3341–3346.
(19) Chaskar, A.; Chen, H.-F.; Wong, K.-T. Bipolar host materials: a chemical approach for highly efficient electrophosphorescent devices. Adv. Mater. 2011, 23, 3876–3895.

(20) Méhes, G.; Goushi, K.; Potscavage, W. J.; Jr; Adachi, C. Influence of host matrix on thermally-activated delayed fluorescence: Effects on emission lifetime, photoluminescence quantum yield, and device performance. Org. Electron. 2014, 15, 2027–2037.

(21) Siboni, H. Z.; Aziz, H. Explaining the different efficiency behaviors of PHOLEDs with/without a hole injection barrier at the hole transport layer/emitter layer interface. Org. Electron. 2013, 14, 2510–2517.

(22) Li, W.; Zhao, J.; Li, L.; Du, X.; Fan, C.; Zheng, C.; Tao, S. Efficient solution-processed blue and white OLEDs based on a high-triplet bipolar host and a blue TADF emitter. Org. Electron. 2018, 58, 276–282.

(23) Liu, Y.; Wei, X.; Li, Z.; Liu, J.; Wang, R.; Hu, X.; Wang, P.; Yamada-Takamura, Y.; Qi, T.; Wang, Y. Highly Efficient, Solution-Processed Organic Light-Emitting Diodes Based on Thermally Activated Delayed-Fluorescence Emitter with a Mixed Polymer Interlayer. ACS Appl. Energy Mater. 2018, 1, 543–551.

(24) Qin, W.; Ding, D.; Liu, J.; Yuan, W. Z.; Hu, Y.; Liu, B.; Tang, B. Z. Biocompatible nanoparticles with aggregation-induced emission characteristics as far-red/near-infrared fluorescent bioprobes for in vitro and in vivo imaging applications. Adv. Funct. Mater. 2012, 22, 771–779.

(25) Lu, H.; Zheng, Y.; Zhao, X.; Wang, L.; Ma, S.; Han, X.; Xu, B.; Tian, W.; Gao, H. Highly Efficient Far Red/Near-Infrared Solid Fluorophores: Aggregation-Induced Emission, Intramolecular Charge Transfer, Twisted Molecular Conformation, and Bioimaging Applications. Angew. Chem., Int. Ed. 2016, 55, 155–159.

(26) Zeng, W.; Lai, H. Y.; Lee, W. K.; Jiao, M.; Shiu, Y. J.; Zhong, C.; Gong, S.; Zhou, T.; Xie, G.; Saras, M. Achieving Nearly 30% External Quantum Efficiency for Orange–Red Organic Light Emitting Diodes by Employing Thermally Activated Delayed Fluorescence Emitters Composed of 1, 8-Naphthalimide-Acridine Hybrids. Adv. Mater. 2018, 30, 1704961.

(27) Li, J.; Nakagawa, T.; MacDonald, J.; Zhang, Q.; Nomura, H.; Miyazaki, H.; Adachi, C. Highly efficient organic light-emitting diode based on a hidden thermally activated delayed fluorescence channel in a heptazine derivative. Adv. Mater. 2013, 25, 3319–3323.

(28) Wang, H.; Xie, L.; Peng, Q.; Meng, L.; Wang, Y.; Yi, Y.; Wang, P. Novel thermally activated delayed fluorescence materials—thioxanthone derivatives and their applications for highly efficient OLEDs. Adv. Mater. 2014, 26, 5198–5204.

(29) Pereira, L. F. Organic Light Emitting Diodes: The Use of Rare Earth and Transition Metals; Pan Stanford: Boca Raton, 2012.

(30) Sun, J. W.; Kim, K.-H.; Moon, C.-K.; Lee, J.-H.; Kim, J.-J. Highly efficient sky-blue fluorescent organic light emitting diode based on mixed cohost system for thermally activated delayed fluorescence emitter (2CzPN). ACS Appl. Mater. Interfaces 2016, 8, 9806–9810.

(31) Kumar, M.; Pereira, L. Effect of the Host on Deep-Blue Organic Light Emitting Diodes Based on a TADF Emitter for Roll-Off Supressing. Nanomaterials 2019, 9, 1307.

(32) Lian, J.-R.; Niu, F.-F.; Liu, Y.-W.; Zeng, P.-J. Improved hole-blocking and electron injection using a TPBI Interlayer at the cathode interface of OLEDs. Chin. Phys. Lett. 2011, 28, 047803.

(33) Sasabe, H.; Kido, J. Recent progress in phosphorescent organic light-emitting devices. Eur. J. Org. Chem. 2013, 7653–7663.

(34) Adachi, C.; Baldo, M. A.; Forrest, S. R.; Thompson, M. E. High-efficiency organic electrophosphorescent devices with tris (2-phenylpyridine) iridium doped into electron-transporting materials. Appl. Phys. Lett. 2000, 77, 904–906.

(35) Huang, J.; Pfeiffer, M.; Werner, A.; Blochwitz, J.; Leo, K.; Liu, S. Low-voltage organic electroluminescent devices using pin structures. Appl. Phys. Lett. 2002, 80, 139–141.

(36) Huang, J.; Li, G.; Wu, E.; Xu, Q.; Yang, Y. Achieving high-efficiency polymer white-light-emitting devices. Adv. Mater. 2006, 18, 114–117.

(37) Cai, M.; Xiao, T.; Hellrich, E.; Chen, Y.; Shinar, R.; Shinar, J. High-efficiency solution-processed small molecule electrophosphorescent organic light-emitting diodes. Adv. Mater. 2011, 23, 3590–3596.

(38) Li, Y.; Liu, J.-Y.; Zhao, Y.-D.; Cao, Y.-C. Recent advancements of high efficient donor-acceptor type blue small molecule applied for OLEDs. Mater. Today 2017, 20, 258–266.

(39) Dias, F. B.; Bourdakos, K. N.; Jankus, V.; Moss, K. C.; Kamtekar, K. T.; Bhalla, V.; Santos, J.; Bryce, M. R.; Monkon, A. P. Triplet harvesting with 100% efficiency by way of thermally activated delayed fluorescence in charge transfer OLED emitters. Adv. Mater. 2013, 25, 3707–3714.

(40) Yang, M.-J.; Tsutsui, T. Use of Poly(9-vinylcarbazole) as Host Material for Iridium Complexes in High-Efficiency Organic Light-Emitting Devices. Jpn. J. Appl. Phys., Part 1 2000, 39, L828.

(41) Chang, S.-C.; He, G.; Chen, F.-C.; Guo, T.-F.; Yang, Y. Degradation mechanism of phosphorescent-dye-doped polymer light-emitting diodes. Appl. Phys. Lett. 2001, 79, 2088–2090.

(42) Gill, W. D. Drift mobilities in amorphous charge-transfer complexes of trinitrofluorenone and poly-n-vinylcarbazole. J. Appl. Phys. 1972, 43, 5033–5040.

(43) Kawamura, Y.; Yanagida, S.; Forrest, S. R. Energy transfer in polymer electrophosphorescent light emitting devices with single and multiple doped luminescent layers. J. Appl. Phys. 2002, 92, 87–93.

(44) Jou, J.-H.; Wang, W.-B.; Chen, S.-Z.; Shye, J.-J.; Hu, M.-F.; Lin, C.-W.; Shen, S.-M.; Wang, C.-J.; Liu, C.-P.; Chen, C.-T.; Wu, M.-F.; Liu, S.-W. High-efficiency blue organic light-emitting diodes using a 3, 5-di (9H-carbazol-9-yl) phenalenylsilane host via a solution-process. J. Mater. Chem. 2010, 20, 8411–8416.

(45) Kim, D.; Coropceanu, V.; Brédas, J.-L. Design of efficient ambipolar host materials for organic blue electrophosphorescence: theoretical characterization of hosts based on carbazole derivatives. J. Am. Chem. Soc. 2011, 133, 17985–17990.

(46) May, F.; Al-Helwi, M.; Baumeier, B.; Kowalsky, W.; Fuchs, E.; Lennartz, C.; Andrienko, D. Design rules for charge-transport efficient host materials for phosphorescent organic light-emitting diodes. J. Am. Chem. Soc. 2012, 134, 13818–13822.

(47) Liu, S.-W.; Lee, J.-H.; Lee, C.-C.; Chen, C.-T.; Wang, J.-K. Charge carrier mobility of mixed-layer organic light-emitting diodes. Appl. Phys. Lett. 2007, 91, 142106.

(48) Hung, W.-Y.; Ke, T.-H.; Lin, Y.-T.; Wu, C.-C.; Hung, T.-H.; Chao, T.-C.; Wong, K.-T.; Wu, C.-I. Employing ambipolar oligofluorene as the charge-generation layer in time-of-flight mobility measurements of organic thin films. Appl. Phys. Lett. 2006, 88, 064102.

(49) Kim, H. S.; Park, S.-R.; Suh, M. C. Concentration Quenching Behavior of Thermally Activated Delayed Fluorescence in a Solid Film. J. Phys. Chem. C 2017, 121, 13986–13997.

(50) Jou, J.-H.; Shen, S.-M.; Lin, C.-R.; Wang, Y.-S.; Chou, Y.-C.; Chen, S.-Z.; Jou, Y.-C. Efficient very-high color rendering index organic light-emitting diode. Org. Electron. 2011, 12, 865–868.

(51) Giebeler, C.; Antoniadis, H.; Bradley, D. D. C.; Shirota, Y. Influence of the hole transport layer on the performance of organic light-emitting diodes. J. Appl. Phys. 1999, 85, 608–615.

(52) Cao, S.; Prasad, R.; Anand, R. The Effect of Spatially Distributed Electron and Hole Blocking Layers on the Characteristics of OLEDs. 2007 International Workshop on Physics of Semiconductor Devices; IEEE, 2007, pp 634–636.

(53) Jesuraj, P. J.; Hafeez, H.; Kim, D. H.; Lee, J. C.; Lee, W. H.; Cho, D. K.; Kim, C. H.; Song, M.; Kim, C. S.; Ryu, S. Y. Recombination zone control without sensing layer and the exciton confinement in green phosphorescent OLEDs by excluding interface energy transfer. J. Phys. Chem. C 2018, 122, 2951–2958.