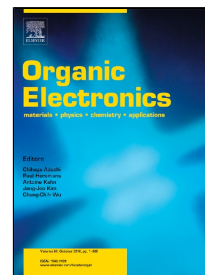


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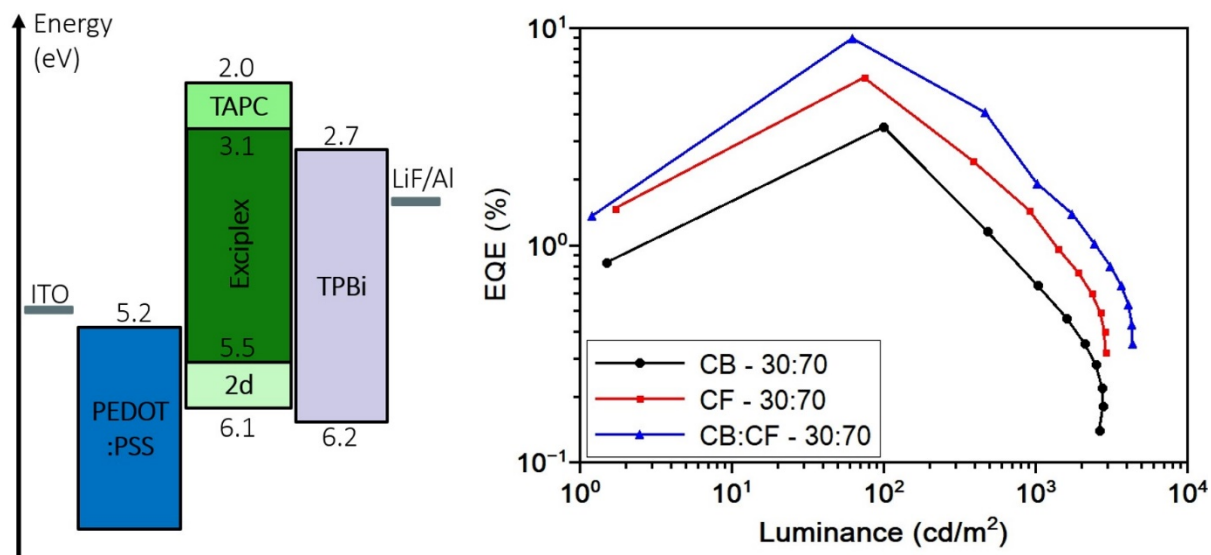
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Graphical abstract

Solution processable small molecule based TADF exciplex OLEDs



Solution processable small molecule based TADF exciplex OLEDs

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Abstract

In this work we report the optimisation of the solution processable TADF exciplex emitter in OLED devices formed by the small molecules 9-[2,8]-9-carbazole-[dibenzothiophene-*S,S*-dioxide]-carbazole (**DCz-DBTO2**) and 4,4'-cyclohexylidenebis[*N,N*-bis(4-methylphenyl)benzenamine] (**TAPC**). This exciplex, previously reported by Jankus et al. [1], has gave vacuum deposited devices having respectively current efficiency, power efficiency and EQE of 32.3 cd/A, 26.7 lm/W and 10.3 % obtained for with DCz-DBTO2:TAPC wt% ratio of 30:70. In this work we optimised the thickness and ratio of the exciplex layer using two different solvents, chlorobenzene and chloroform. The best results were achieved when the two solvents were mixed, adding 5 vol% of chlorobenzene to chloroform. With this solvent mixture comparable results to evaporated devices were achieved, 27.5 ± 3.5 cd/A, 16.5 ± 2.0 lm/W and EQE of 8.9 ± 0.6 % at the same DCz-DBTO2:TAPC wt% ratio of 30:70, demonstrating the suitability of small molecule TADF exciplexes as solution processable emissive layer for OLEDs.

1. Introduction

OLED technology represents the present and future of the display and lightening industry. OLEDs have the advantage of being able to be deposited on flexible substrates as well offering very good colour purity and low power consumption. [2,3]

Generally, there are two approaches to fabricate OLEDs, one is via vacuum deposition while the other is by solution processing. The first offers great control over the deposition process and complex multilayer fabrication that often results in more efficient and stable devices. Characteristics that have led to evaporated OLEDs dominating the present markets. On the other hand, this technique needs to be performed under costly high vacuum conditions and the usage of material can be far greater than in solution processing, which is a very important aspect when mass production is taken into consideration. For this reason, efficient solution processable OLEDs are still of great interest and need to be designed in order to be integrated in solution based roll-to-roll deposition systems to lower the production costs. [4]

For this reason, an important task is to obtain comparable devices from solution processing to those obtained via thermal evaporation. Good results have been achieved with solution processed phosphorescent OLEDs (PHOLEDs). [5,6] In recent years thermally activated fluorescence (TADF) has also been used to enhance the efficiency of the OLEDs. TADF also allows the harvesting of 100% of the excitons produced by the electrical excitation in the device by up-converting the triplets back to singlets via reverse intersystem crossing (rISC).[7,8] TADF can be obtained in small molecules but also in exciplexes [9–11] via the same mechanism [12]. Very good results have been achieved with both small molecules and exciplexes with EQE of the devices close to 20% for blue, green and red.[13–16]

Good results have been obtained also via solution processing TADF small molecules and TADF exciplex hosts doped with fluorescent or phosphorescent emitters. [17–22] Here we demonstrate excellent efficiency from a simple TADF exciplex layer acting as the emitter in a device.

In this work, we solution processed the TADF exciplex formed by the D-A-D molecule 9-[2,8]-9-carbazole-[dibenzothiophene-*S,S*-dioxide]-carbazole (**DCz-DBTO2**) and 4,4'-cyclohexylidenebis[*N,N*-bis(4-methylphenyl)benzenamine] (**TAPC**). We have chosen this exciplex because it has already been demonstrated to harvest nearly 100% of the triplets via TADF with a PLQY of 53 ± 4 % in a co-evaporated film with a 30%wt of DCz-DBTO2 in TAPC. [1]

Both molecules have good solubility in chlorinated solvents (>20 mg mL⁻¹) such as Chlorobenzene (**CB**) and Chloroform (**CF**). We optimised the deposition parameters to maximise the OLED performances obtaining a maximum current efficiency of 27.5 ± 3.5 cd/A, a maximum power efficiency of 16.5 ± 2.0 lm/W, a maximum EQE of 8.9 ± 0.6 and luminances > 4000 cd/m² obtaining comparable results to the evaporated devices published by Jankus et al. of 32.3 cd/A, 26.7 lm/W and 10.3 % for a device with the same DCz-DBTO2:TAPC wt% of 30:70 [1] We explored the effect of the thickness and DCz-DBTO2:TAPC ratio in both solvents and used the two solvent mixed together with a ratio of CB:CF 5:95 vol% as this has been shown to be an effective solvent blend to obtain the best wettability offered by the CF with an improved surface tension provided by the CB. [23,24]

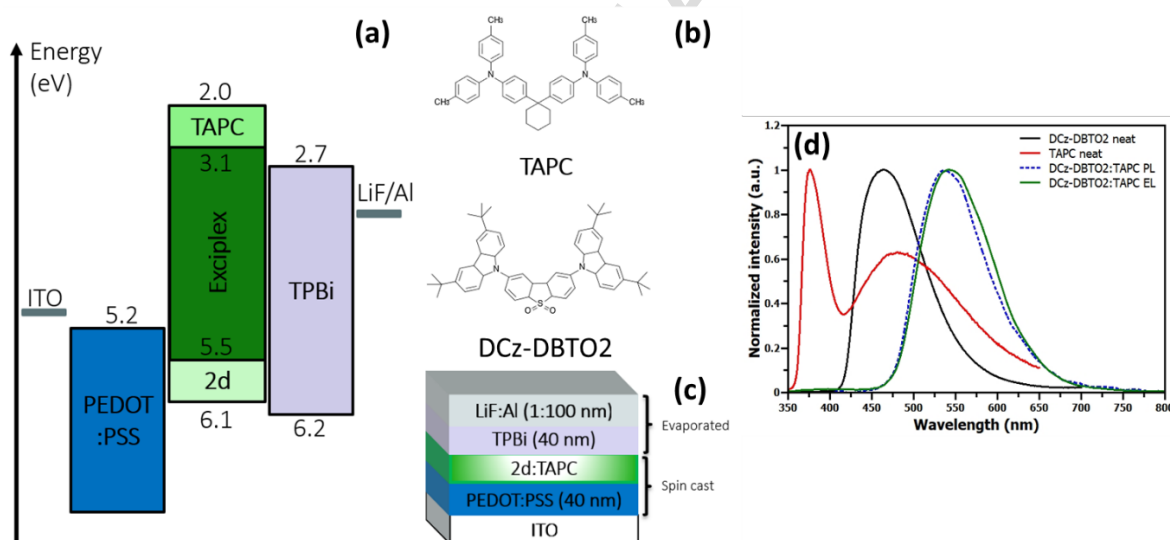


Figure 1. (a) The energy diagrams of the devices produced in this study. (b) The molecular structures of TAPC and DCz-DBTO2. (c) the device structure of the devices used in this work. The PEDOT:PSS and the DCz-DBTO2:TAPC layer have been deposited via spin coating while TPBi and the cathode via thermal evaporation. (d) Normalised photoluminescence of DCz-DBTO2, TAPC, DCz-DBTO2:TAPC thin films and electroluminescence spectrum of the DCz-DBTO2:TAPC used as EML in the OLED devices. The red-shifted peak in the TAPC fluorescence spectrum it is assigned to excimers formed in solid state.

2. Material and Methods

2.1. Materials

4,4'-cyclohexylidenebis[*N,N*-bis(4-methylphenyl)benzenamine] (TAPC), 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) TPBi and PEDOT:PSS Heraeus Clevis A14083 were obtained from Ossila. Lithium Fluoride (LiF) and Aluminum were purchased from Kurt J. Lesker. All solvents were bought from Sigma Aldrich. The patterned ITO substrates, UV curable epoxy and encapsulation coverslips were bought from Ossila. DCz-DBTO2 was synthesized according to procedure described by Vybornyi et al.[25] which improved the original synthetic procedure. [26] All organic materials were sublimed before use.

2.2. Device fabrication

OLED devices were fabricated with a ITO|PEDOT:PSS (40 nm)| DCz-DBTO2:TAPC %wt (x nm)|TPBi (40 nm)|LiF (1 nm)|Al (100 nm). The substrates were sequentially cleaned in an ultra-sonic bath containing Hellmanex solution, 2-propanol (IPA) and 10 vol% NaOH water solution and UV Ozone treated for 5 min. Prior to deposition the PEDOT:PSS (A14083) was filtered with a 0.45 μm PVDF filter. A 40 nm layer of PEDOT:PSS (HIL) was spin cast dynamically at 5000 rpm and annealed at 150°C for 10 min. Afterwards substrates have been moved inside a nitrogen filled glovebox and annealed again for 10 min at 150°C and cooled down prior the deposition of the active layer. The DCz-DBTO2:TAPC (EML) layer was then spin coated on top of the PEDOT:PSS from chloroform, chlorobenzene or a 5:95 chlorobenzene:chloroform solvent blend, all solutions were filtered using 0.1 μm PTFE filter. No thermal anneal was performed for the EML. The thickness of the films deposited were measured with a VASE ellipsometer. The substrates were then loaded into an evaporation chamber, without exposing them to air and left in high vacuum overnight. Without breaking the vacuum, at pressure $< 5 \times 10^{-6}$ mBar, a 40 nm TPBi (ETL) layer was deposited followed by 1 nm LiF and 100 nm Al. Before testing the devices were encapsulated in the glovebox. The encapsulation was performed using a glass coverslip sealed by applying a drop of a low viscosity UV curable epoxy to cover the entire active area of the device. Afterward the encapsulated devices were exposed to UV light for 15 minutes.

2.3. Device measurement

The PL and EL spectra were collected using a BLUE-Wave vis-25 spectrometer. For the PL measurements the films were excited using a 280 nm LED. OLED current density and voltage were

measured using an Ossila Source Measure Unit-X100 while the luminance was collected using a Konica Minolta LS-110 luminance meter. Power efficiency and EQE were calculated assuming Lambertian emission profile.

3. Results and discussion

3.1. EML processed from Chlorobenzene

3.1.1. Thickness

Figure 2 shows the results obtained for devices with the structure ITO|PEDOT:PSS 40 nm| DCz-DBTO2:TAPC (30:70 x nm)|TPBi 40 nm|LiF 1nm|Al 100 nm. This ratio between DCz-DBTO2 and TAPC was chosen as a starting point for the study because it has shown to give the highest values of current and power efficiency in the evaporated devices.[1] The thickness of the EML was varied from 15 to 48 nm, the results are summarised in Table 1. It is clear, in Figure 2a, that increasing the EML thickness from 15 to 20 nm does not substantially increase the resistivity of the devices and all the efficiency values remain constant within the standard deviations as well as the turn on voltage (V_{ON}) around 3.5 V. When the EML thickness is further increased to 24 and 34 nm, the resistivity of the device increased, as well V_{ON} becomes 4 V. In terms of efficiency, the greater EML thickness does not substantially vary the maximum efficiency, which is reached around 100 cd/m². Surprisingly, the efficiency of the OLEDs does not change substantially either with all the maximum CE, mean values being within 10 ± 2 cd/A. The EQE as well can be assumed constant considering the standard deviations to be 3 ± 0.9 %.

It's worth mentioning that the efficiency of the device with the EML thickness of 48 nm is the lowest at low luminance due to some current leakage visible in Figure 2a. This leakage is probably caused by the low spin speed used to deposit the DCz-DBTO2:TAPC layer, 500 rpm.[27–29] Using a low spin speed might also have caused an increase on the roughness of the film that can affect the conduction of the device.[30]

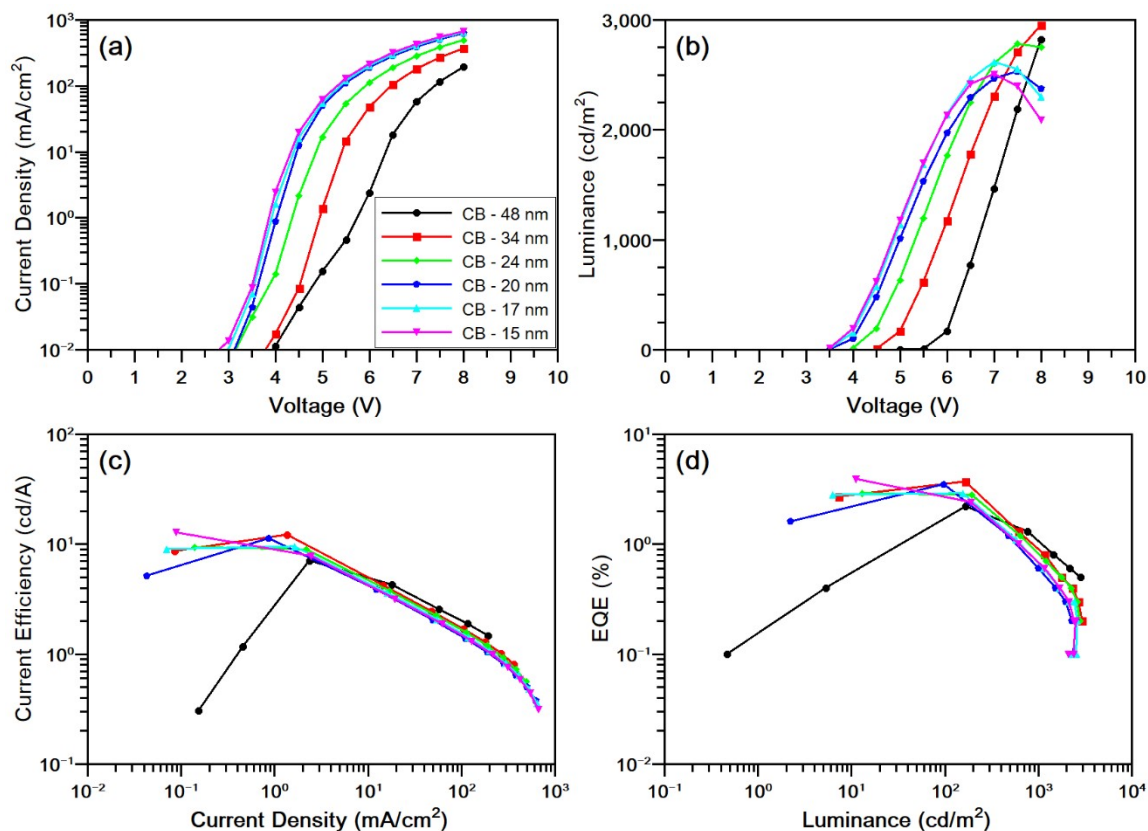


Figure 2. Device characteristics for ITO|PEDOT:PSS (40 nm)|DCz-DBTO2:TAPC 30:70 (15-17-20-24-34-48 nm)|TPBi (40 nm)|LiF (1 nm)|Al (100 nm) deposited from chlorobenzene. **(a)** Current density vs driving voltage. **(b)** Luminance vs driving voltage. **(c)** Current efficiency vs current density. **(d)** Power efficiency vs Luminance.

Table 1. Summary of results obtained for OLEDs produced with the structure ITO|PEDOT:PSS (40 nm)|DCz-DBTO2:TAPC 30:70 (15-17-20-24-34-48 nm)|TPBi (40 nm)|LiF (1 nm)|Al (100 nm) deposited from chlorobenzene.

	48 nm	34 nm	24 nm	20 nm	17 nm	15 nm
Max CE (cd/A)	6.5 ± 2.2	11.1 ± 2.2	7.8 ± 2.0	11.5 ± 0.8	9.3 ± 0.7	12.3 ± 1.9
Max PE (lm/W)	3.4 ± 1.2	7.1 ± 1.4	6.0 ± 1.5	9.1 ± 0.6	7.4 ± 0.6	11.0 ± 1.7
Max EQE (%)	2.1 ± 0.5	3.4 ± 0.7	2.4 ± 0.6	3.5 ± 0.2	2.8 ± 0.2	3.7 ± 0.6
Max Luminance (cd/m²)	3033 ± 105	3296 ± 240	2787 ± 192	2436 ± 214	2566 ± 157	2254 ± 250
V_{ON} @ 1cd/m² (V)	5 ± 0.5	4 ± 0.5	4 ± 0.5	3.5 ± 0.5	3.5 ± 0.5	3.5 ± 0.5

3.1.2. DCz-DBTO2 and TAPC Ratio

To optimise the ratio between the two exciplex forming molecules the same device structure has been used. We fixed the EML layer to 20 nm since is the thickness that has given the second highest CE and EQE value with the smallest standard deviation to ensure consistency in the processing. The ratio

between DCz-DBTO2 and TAPC has then been varied from 10:90 to 50:50 wt% and the results are summarised in Table 2.

In Figure 3a is visible that the variation of DCz-DBTO2:TAPC ratio has no effect on the JV characteristics of the devices passing from a 20:80 wt% to 50:50 wt% ratio. Only the 10:90 wt% ratio shows a slightly lower current likely due to the little amount of DCz-DBTO2 conducting electrons from the TPBi into the EML in agreement with what shown by Jankus et al. [1] On the other hand in Figure 3b is shown as is the 10:90 ratio to achieve the highest maximum brightness despite having only 10 wt% of DCz-DBTO2. It is interesting also that the maximum brightness monotonically diminishes with the increasing of DCz-DBTO2 percentage in the EML. This is attributed to an increased leakage of electrons with the DCz-DBTO2 loading since no electron blocking layer (EBL) is present between the PEDOT:PSS layer and the EML in the OLED stack.

In terms of efficiency, as visible in Table 2, surprisingly the highest values are achieved for the two extreme ratios, 10:90 and 50:50. On the other hand, as shown in Figure 3. and 3d the devices where 50:50 wt% was utilised showed their efficiency peak at very low current density and luminance. The other ratios instead show the maximum efficiency at values around 100 cd/m² that represents the operational value used as reference for display application. This behaviour can be explained considering that increasing the DCz-DBTO2 doping level moves the recombination zone towards the HIL balancing the charges at lower current density values than for the ratios where less DCz-DBTO2 is present.

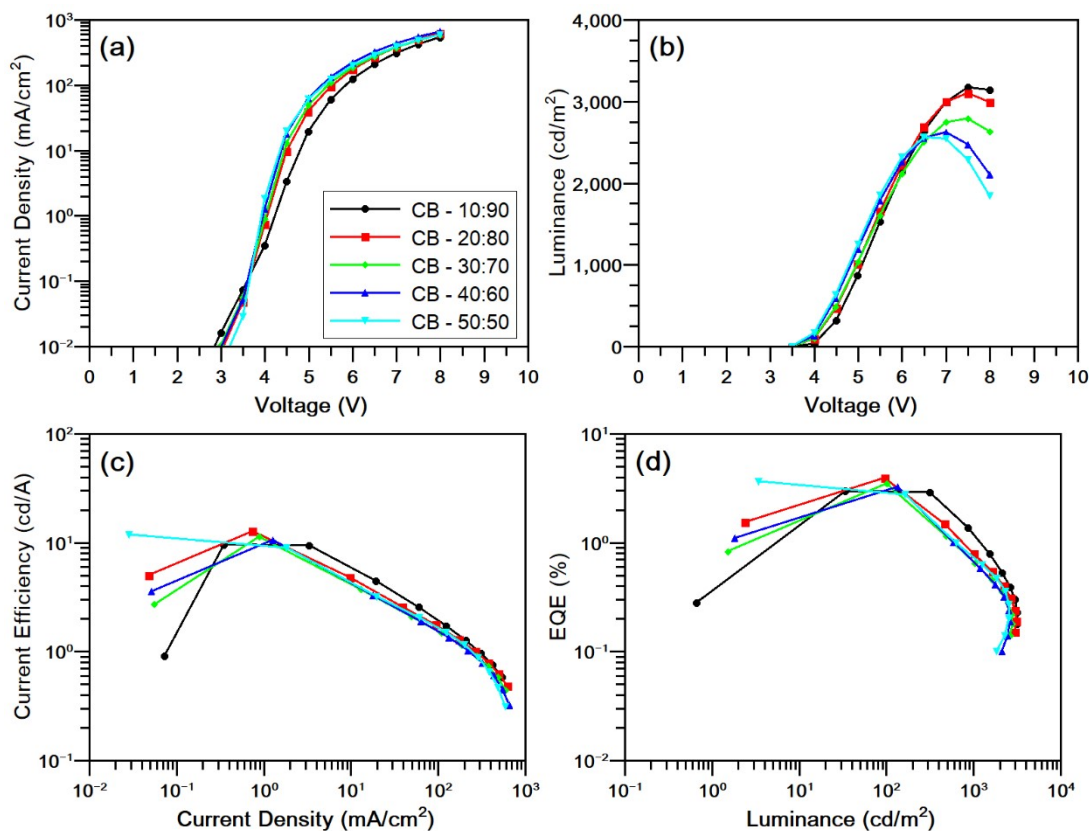


Figure 3. Device characteristics for structure ITO|PEDOT:PSS (40 nm)| DCz-DBTO2:TAPC 10:90-20:80-30:70-40:60-50:50 (20 nm)|TPBi (40 nm)|LiF (1 nm)|Al (100 nm) deposited from chlorobenzene. (a) Current density vs driving voltage. (b) Luminance vs driving voltage. (c) Current efficiency vs current density. (d) Power efficiency vs Luminance.

Table 2. Summary of results obtained for OLEDs produced with the structure ITO|PEDOT:PSS (40 nm)|DCz-DBTO2:TAPC 10:90-20:80-30:70-40:60-50:50 (60 nm)|TPBi (40 nm)|LiF (1 nm)|Al (100 nm) deposited from chlorobenzene.

	10:90	20:80	30:70	40:60	50:50
Max CE (cd/A)	14.2 ± 3.4	11.6 ± 1.2	13.0 ± 2.6	11.7 ± 1.0	14.1 ± 2.5
Max PE (lm/W)	11.2 ± 2.7	9.1 ± 0.9	10.2 ± 2.0	9.2 ± 0.8	12.7 ± 2.2
Max EQE (%)	4.3 ± 1.0	3.5 ± 0.4	3.9 ± 0.8	3.5 ± 0.3	4.2 ± 0.8
Max Luminance (cd/m²)	3200 ± 165	2876 ± 200	2786 ± 146	2583 ± 126	2449 ± 139
V_{ON} @ 1cd/m² (V)	3.5 ± 0.5	3.5 ± 0.5	3.5 ± 0.5	3.5 ± 0.5	3.5 ± 0.5

3.2. EML processed from Chloroform

Since the efficiency was not high enough (EQE < 5%) when processing from CB we tried to process from CF as it provides better wettability and his very low surface tension allows to solidify the film onto the substrate much faster than CB. [31]

3.2.1. Thickness

At first, as previously shown for the CB devices, the influence of the EML thickness has been studied when spin cast from CF. Figure 4 shows that increasing the EML thickness increases monotonically the resistivity of the device. The devices with a 50 nm EML showed the highest CE, PE and EQE mean value, 17.3 ± 2.7 cd/A, 10.9 ± 1.7 lm/W and 5.2 ± 0.8 % respectively. The highest average maximum brightness is $3,982 \pm 312$ cd/m² and was achieved for the devices with the EML 60 nm thickness. When comparing devices produced with similar EML, table 1 and table 3 higher maximum brightness are consistently obtained from devices where CF was used to deposit the EML rather than CB as well as higher efficiency. This discrepancy can be explained considering the reduced drying time achieved when spin casting the devices using CF solutions. This dries the solution on the substrate in less than 1 second minimising the π - π stacking of the carbazoles on the DCz-DBTO2 molecules. [32,33]

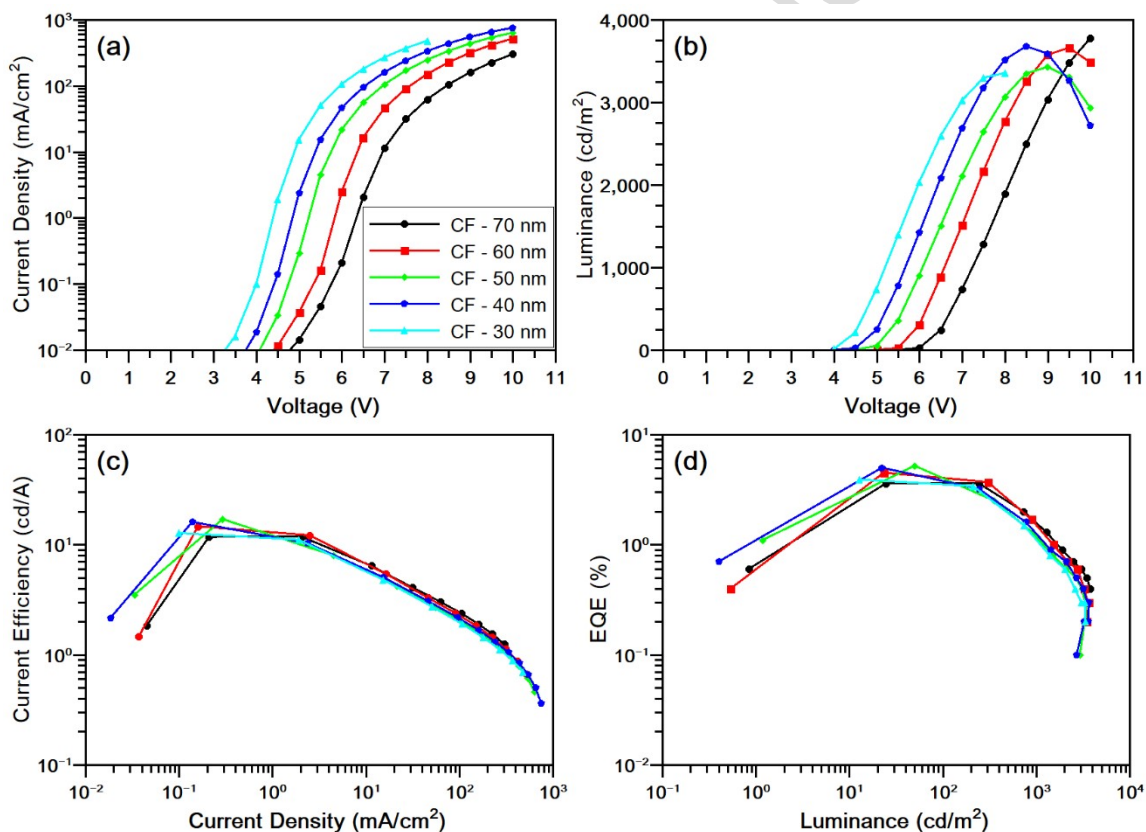


Figure 4. Device characteristics for ITO|PEDOT:PSS (40 nm)|DCz-DBTO2:TAPC 30:70 (30-40-50-60-70 nm)|TPBi (40 nm)|LiF (1 nm)|Al (100 nm) deposited from chloroform. **(a)** Current density vs driving voltage. **(b)** Luminance vs driving voltage. **(c)** Current efficiency vs current density. **(d)** Power efficiency vs Luminance.

Table 3. Summary of results obtained for OLEDs produced with the structure ITO|PEDOT:PSS (40 nm)|DCz-DBTO2:TAPC 30:70 (30-40-50-60-70 nm)|TPBi (40 nm)|LiF (1 nm)|Al (100 nm) deposited from chloroform.

	70 nm	60 nm	50 nm	40 nm	30 nm
Max CE (cd/A)	12.9 ± 2.1	14.1 ± 2.3	17.3 ± 2.7	14.7 ± 3.2	13.0 ± 2.7
Max PE (lm/W)	6.6 ± 1.2	7.6 ± 1.4	10.9 ± 1.7	10.2 ± 2.2	9.8 ± 2.4
Max EQE (%)	3.9 ± 0.6	4.2 ± 0.7	5.2 ± 0.8	5.1 ± 0.8	4.0 ± 0.8
Max Luminance (cd/m²)	3,533 ± 593	3,982 ± 312	3,816 ± 315	3,454 ± 280	3,272 ± 216
V_{ON} @ 1cd/m² (V)	5.5 ± 0.5	5.5 ± 0.5	4.5 ± 0.5	4.0 ± 0.5	4.0 ± 0.5

3.2.2. DCz-DBTO2 and TAPC Ratio

To get the highest possible film quality to carry out the ratio study we decided to set the spin speed at 6000 rpm and with 20 mg/ml CF solution which deposited a 60 nm DCz-DBTO2:TAPC layer. The ratio between DCz-DBTO2 and TAPC has again being varied between 10:90 and 50:50 wt%. The results show that we obtain similar results in a window of DCz-DBTO2:TAPC ratios from 20:80 to 40:60 as shown in Table 4.

Even considering that there is no massive difference in terms of maximum efficiency mean values for the devices with DCz-DBTO2 content between 20-40 wt%. It is worth noting that the devices with a lower content of DCz-DBTO2 content, 10 and 20 wt%, show a mean value of the maximum EQE of 5.6 % and 6.4 %, respectively, that peaks at 10 cd/m². On the other hand, the devices with DCz-DBTO2 content of 30 and 40 wt% show similar mean values of the maximum EQE of 6.2 % and 6.1 % respectively. This time values are obtained now at 100 cd/m² which represents the brightness reference value for OLED display devices.

In Figure 5a it can be observed that the current increases with increasing DCz-DBTO2 concentration in the blend saturating at a ratio of 30% of DCz-DBTO2 and remains constant for the higher ratios. This can be explained by considering that increasing the DCz-DBTO2 content in the device increases the contribution of the electron current. The luminance also follows a similar trend, as expected the brightness increases with the increasing current reaching a maximum mean value for the 30:70 ratio of 3061 cd/m². The maximum brightness decreases at 50:50 ratio due probably due to DCz-DBTO2 π - π stacking that reduces the probability of exciplex formation and thus the brightness of the device.

The slightly different behaviour observed between the two ratio studies can be attributed to the different EML thicknesses deposited, which is 3 times higher in the films deposited from chloroform than those deposited from chlorobenzene. This leads to a different optimal position of the recombination zone inside the EML.

These results can be compared to those of reported previously by Jankus et al. [1]. The optimum donor acceptor ratio found for more complex devices including exciton blocking layers was found to be 38:62,

yielding devices having respectively current efficiency, power efficiency and EQE of 32.3 cd/A, 26.7 lm/W and 14%. Thus, we see that for the more simple solution processed devices without blocking layers we can match the evaporated devices when optimum charge balance is achieved in the solution processed devices, but with the inclusion of blocking layers in more complex devices structures, this performance can be improved upon. However, the result clearly suggests that by achieving optimal charge balance in solution cast devices, performance levels matching evaporated devices can be achieved in exciplex based TADF devices.

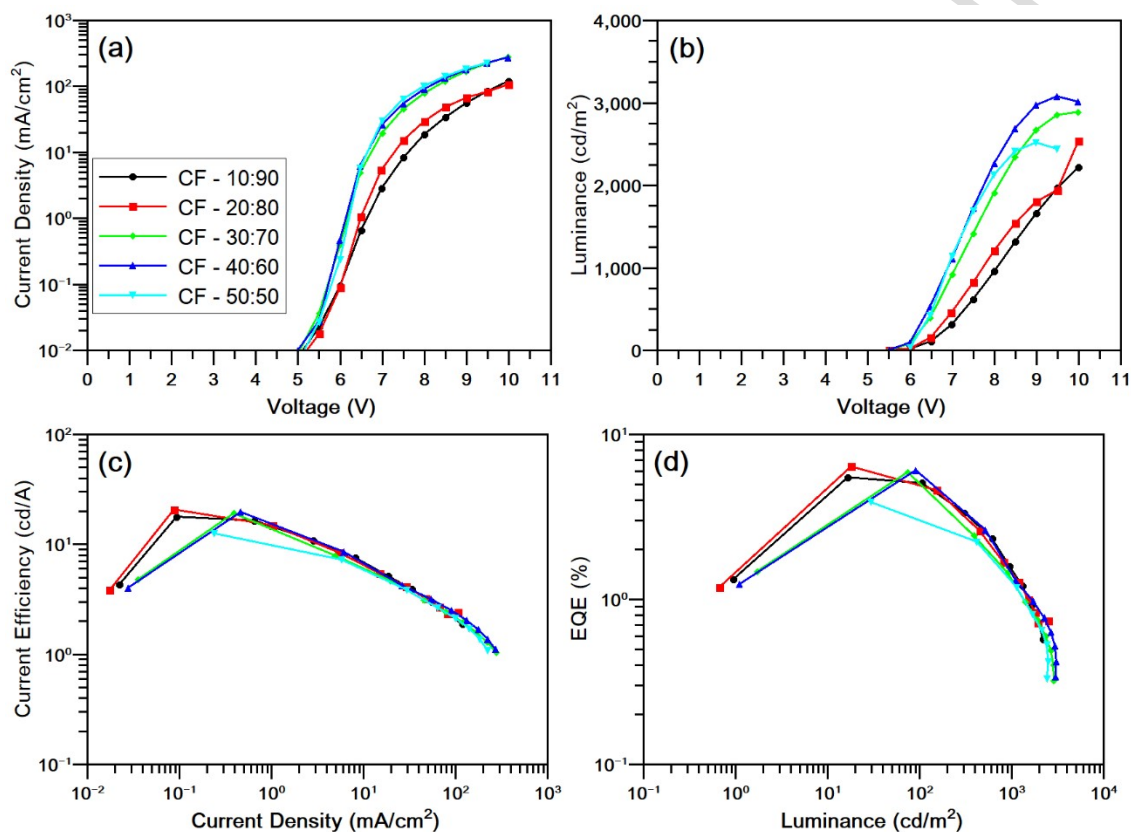


Figure 5. Device characteristics for structure ITO|PEDOT:PSS (40 nm)|DCz-DBTO2:TAPC 10:90-20:80-30:70-40:60-50:50 (60 nm)|TPBi (40 nm)|LiF (1 nm)|Al (100 nm) deposited from chloroform. **(a)** Current density vs driving voltage. **(b)** Luminance vs driving voltage. **(c)** Current efficiency vs current density. **(d)** Power efficiency vs Luminance.

Table 4. Summary of results obtained for OLEDs produced with the structure ITO|PEDOT:PSS (40 nm)|DCz-DBTO2:TAPC 10:90-20:80-30:70-40:60-50:50 (60 nm)|TPBi (40 nm)|LiF (1 nm)|Al (100 nm) deposited from chloroform.

	10:90	20:80	30:70	40:60	50:50
Max CE (cd/A)	18.5 ± 2.6	21.1 ± 7.3	20.7 ± 3.8	19.5 ± 4.0	15.4 ± 4.4
Max PE (lm/W)	9.5 ± 1.2	11.0 ± 3.9	10.9 ± 2	10.2 ± 2.1	7.2 ± 2.7
Max EQE (%)	5.6 ± 0.8	6.4 ± 1.9	6.2 ± 1.4	6.1 ± 1.1	4.1 ± 1.4
Max Luminance (cd/m²)	2210 ± 104	2821 ± 332	3061 ± 131	2998 ± 350	2528 ± 207

V_{ON} @ 1cd/m^2 (V)	6.0 ± 0.5	5.5 ± 0.5	5.5 ± 0.5	5.5 ± 0.5	5.5 ± 0.5
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3.3. EML processed from Chlorobenzene:Chloroform solvent blend

Both optimization studies have shown that the optimal ratio lies between 20:80 and 30:70 and the CF thickness optimization identified 60 nm as optimal. To further improve our processing with added 5 vol% of CB to the CF as it has been shown in the literature that improves the film quality limiting while still limiting the π - π stacking of the carbazoles on the DCz-DBTO2, leading to higher performances. [23,24] With this solvent blend, we optimised again the thickness of the EML maintaining constant the ratio between DCz-DBTO2 and TAPC at 30:70 wt%.

The results, summarised in Table 5, show that the best results are obtained for an EML thickness of 60 nm. This result was expected since the solvent blend is formed by 95% of CF and only 5% of CB and the optimal parameter were likely to be close to the ones obtained for the devices prepared for solutions made with pure CF. Respectively, a maximum CE and EQE of 27.5 ± 3.3 cd/A and 8.9 ± 0.6 % is achieved as well as a maximum brightness close to 5000 cd/m². As seen in Figure 6a, the devices with the EML 15 nm thick have current leakage even at low voltage probably because of pin holes formed due to the low thickness of the layer. A similar problem was also observed for the devices deposited from CB with the same EML thickness.

The resistivity of the OLEDs increases with increase of the EML thickness as expected. Curiously the devices with the 15 nm thick EML show higher brightness than those of 21 nm. This behaviour is attributed to the current leakage present in the latter devices. In the devices with 30 and 60 nm thick EML the brightness increases monotonically with thickness as expected.

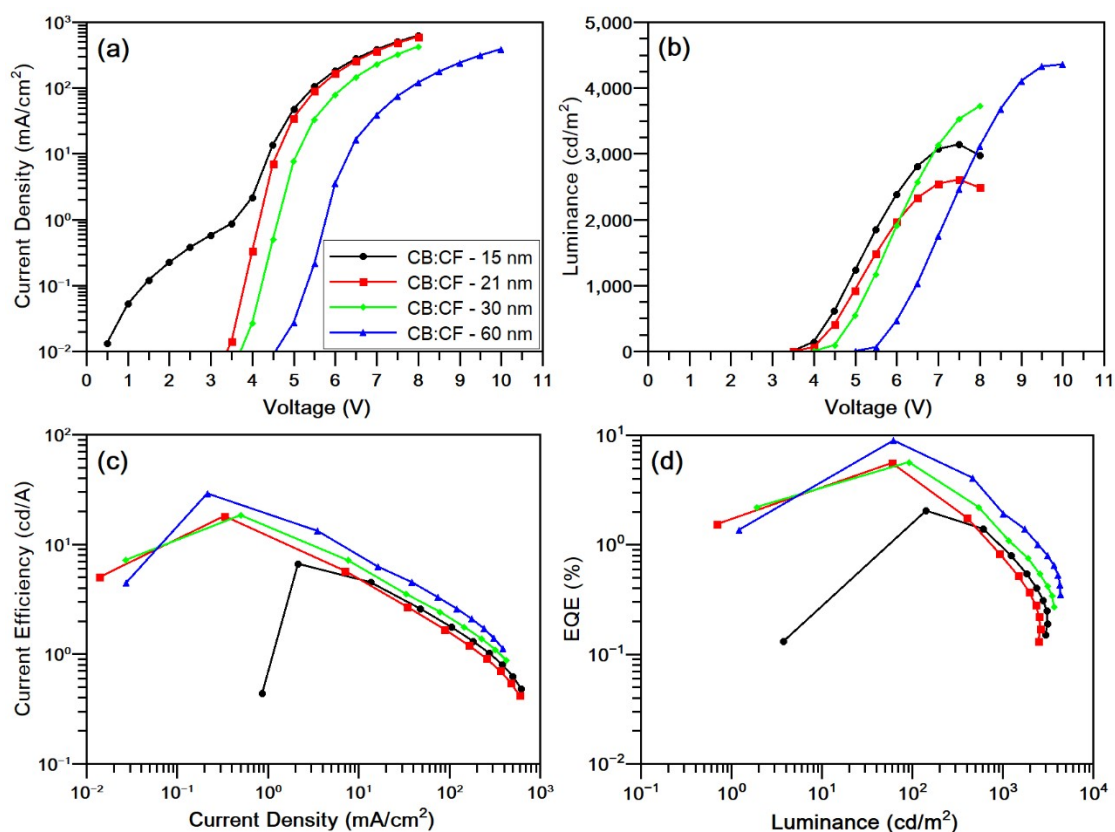


Figure 6. Device characteristics for ITO|PEDOT:PSS (40 nm)|DCz-DBTO2:TAPC 30:70 (15-21-30-60 nm)|TPBi (40 nm)|LiF (1 nm)|Al (100 nm) deposited from a 5:95 chlorobenzene:chloroform solution. **(a)** Current density vs driving voltage. **(b)** Luminance vs driving voltage. **(c)** Current efficiency vs current density. **(d)** Power efficiency vs Luminance.

Table 5. Summary of results obtained for OLEDs produced with the structure ITO|PEDOT:PSS (40 nm)|DCz-DBTO2:TAPC 30:70 (15-21-30-60 nm)|TPBi (40 nm)|LiF (1 nm)|Al (100 nm) deposited from a 5:95 chlorobenzene:chloroform solution.

	60 nm	30 nm	21 nm	15 nm
Max CE (cd/A)	27.5 ± 3.3	18.0 ± 1.0	20.2 ± 2.0	5.9 ± 2.8
Max PE (lm/W)	15.0 ± 1.9	12.6 ± 0.7	15.9 ± 1.2	4.6 ± 2.3
Max EQE (%)	8.9 ± 0.6	5.4 ± 0.4	6.1 ± 0.6	2.7 ± 0.7
Max Luminance (cd/m²)	4679 ± 304	3657 ± 187	2992 ± 280	3020 ± 142
V_{ON} @ 1cd/m² (V)	5.5 ± 0.5	4.0 ± 0.5	3.5 ± 0.5	3.5 ± 0.5

4. Conclusion

We have successfully demonstrated the feasibility of solution depositing TADF exciplexes as emissive layers in solution processed hybrid OLEDs using the DCz-DBTO2:TAPC TADF exciplex as an EML. The effect on the performance of the devices with the variation of the EML thickness and DCz-DBTO2:TAPC ratio has been systematically studied for devices prepared from chlorobenzene,

chloroform and 5:95 vol% blend of chlorobenzene:chloroform. With the solvent blend, comparable results to those obtained by evaporation deposition by Jankus et al [1] has been achieved in terms of brightness, current efficiency, power efficiency and EQE. The best result obtained in this work is 27.5 ± 3.3 cd/A with a maximum brightness of 4679 ± 304 cd/m² and EQE of $8.9 \pm 0.6\%$, at the same DCz-DBTO2:TAPC wt% ratio of 30:70. We are confident that this result can be improved through further optimization of the device stack by introducing electron and hole blocking layers for better confinement of carriers within the exciplex for example.

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References

- [1] V. Jankus, P. Data, D. Graves, C. McGuinness, J. Santos, M.R. Bryce, F.B. Dias, A.P. Monkman, Highly efficient TADF OLEDs: How the emitter-host interaction controls both the excited state species and electrical properties of the devices to achieve near 100% triplet harvesting and high efficiency, *Adv. Funct. Mater.* 24 (2014) 6178–6186. doi:10.1002/adfm.201400948.
- [2] M. Hack, M.S. Weaver, J.J. Brown, Status and Opportunities for Phosphorescent OLED Lighting, *SID.* (2017) 187–190.
- [3] Y. Lin, M. Lee, A.T. Huang, Booming Flexible Applications Enabled by AMOLED Technologies, *SID.* (2017) 29–32.
- [4] F.C. Krebs, R.R. Søndergaard, H. Markus, Roll-to-Roll Fabrication of Large Area Functional Organic Materials, (2013) 16–34. doi:10.1002/polb.23192.
- [5] C.W. Lee, J.Y. Lee, High Quantum Efficiency in Solution and Vacuum Processed Blue Phosphorescent Organic Light Emitting Diodes Using a Novel Benzofuropyridine-Based Bipolar Host Material, *Adv. Mater.* 25 (2013) 596–600. doi:10.1002/adma.201203180.
- [6] W. Lin, W. Huang, M. Huang, C. Fan, H.-W. Lin, L.-Y. Chen, J.-S. Liu, T.-C. Chao, M.-R. Tseng, A bipolar host containing carbazole/dibenzothiophene for efficient solution-processed blue and white phosphorescent OLEDs, *J. Mater. Chem. C.* 1 (2013) 6835–6841. doi:10.1039/c3tc31357c.
- [7] Y. Tao, K. Yuan, T. Chen, P. Xu, H. Li, R. Chen, C. Zheng, L. Zhang, W. Huang, Thermally Activated Delayed Fluorescence Materials Towards the Breakthrough of Organoelectronics, *Adv. Mater.* 26 (2014) 7931–7958. doi:10.1002/adma.201402532.
- [8] F.B. Dias, T.J. Penfold, A.P. Monkman, Photophysics of thermally activated delayed fluorescence molecules, *Methods Appl. Fluoresc.* 5 (2017) 012001. doi:10.1088/2050-6120/aa537e.
- [9] L. Song, Y. Hu, Z. Liu, Y. Lv, X. Guo, X. Liu, Harvesting triplet excitons with exciplex thermally activated delayed fluorescence emitters toward high performance heterostructured organic light-emitting field effect transistors, *ACS Appl. Mater. Interfaces.* 9 (2017) 2711–2719. doi:10.1021/acsami.6b13405.
- [10] K. Goushi, K. Yoshida, K. Sato, C. Adachi, Organic light-emitting diodes employing efficient

- reverse intersystem crossing for triplet-to-singlet state conversion, *Nat. Photonics*. 6 (2012) 253–258. doi:10.1038/nphoton.2012.31.
- [11] D. Graves, V. Jankus, F.B. Dias, A. Monkman, Photophysical Investigation of the Thermally Activated Delayed Emission from Films of m-MTDATA:PBD Exciplex, *Adv. Funct. Mater.* 24 (2014) 2343–2351. doi:10.1002/adfm.201303389.
- [12] P.L. Dos Santos, F.B. Dias, A.P. Monkman, Investigation of the Mechanisms Giving Rise to TADF in Exciplex States, *J. Phys. Chem. C*. 120 (2016) 18259–18267. doi:10.1021/acs.jpcc.6b05198.
- [13] P.L. dos Santos, J.S. Ward, M.R. Bryce, A.P. Monkman, Using Guest–Host Interactions To Optimize the Efficiency of TADF OLEDs, *J. Phys. Chem. Lett.* 7 (2016) 3341–3346. doi:10.1021/acs.jpcclett.6b01542.
- [14] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, Highly efficient organic light-emitting diodes from delayed fluorescence., *Nature*. 492 (2012) 234–8. doi:10.1038/nature11687.
- [15] S. Hirata, Y. Sakai, K. Masui, H. Tanaka, S.Y. Lee, H. Nomura, N. Nakamura, M. Yasumatsu, H. Nakanotani, Q. Zhang, K. Shizu, H. Miyazaki, C. Adachi, Highly efficient blue electroluminescence based on thermally activated delayed fluorescence., *Nat. Mater.* 14 (2015) 330–6. doi:10.1038/nmat4154.
- [16] P. Data, P. Pander, M. Okazaki, Y. Takeda, S. Minakata, A.P. Monkman, Dibenzo[a,j]phenazine-Cored Donor-Acceptor-Donor Compounds as Green-to-Red/NIR Thermally Activated Delayed Fluorescence Organic Light Emitters, *Angew. Chemie - Int. Ed.* 55 (2016) 5739–5744. doi:10.1002/anie.201600113.
- [17] Y.H. Kim, C. Wolf, H. Cho, S.H. Jeong, T.W. Lee, Highly Efficient, Simplified, Solution-Processed Thermally Activated Delayed-Fluorescence Organic Light-Emitting Diodes, *Adv. Mater.* 28 (2016) 734–741. doi:10.1002/adma.201504490.
- [18] Y. Li, G. Xie, S. Gong, K. Wu, C. Yang, Dendronized delayed fluorescence emitters for non-doped, solution-processed organic light-emitting diodes with high efficiency and low efficiency roll-off simultaneously: two parallel emissive channels, *Chem. Sci.* 7 (2016) 5441–5447. doi:10.1039/C6SC00943C.
- [19] Y. Zhang, B. Wang, Y. Yuan, Y. Hu, Z. Jiang, L. Liao, Solution-Processed Thermally Activated Delayed Fluorescence Exciplex Hosts for Highly Efficient Blue Organic Light-Emitting Diodes, *Adv. Opt. Mater.* 5 (2017) 1700012. doi:10.1002/adom.201700012.

- [20] T.-H. Han, M. Choi, C. Jeon, Y. Kim, S. Kwon, T. Lee, Ultrahigh-efficiency solution-processed simplified small-molecule organic light-emitting diodes using universal host materials, *Sci. Adv.* 2 (2016) e1601428.
- [21] L. Duan, L. Hou, T.-W. Lee, J. Qiao, D. Zhang, G. Dong, L. Wang, Y. Qiu, Solution processable small molecules for organic light-emitting diodes, *J. Mater. Chem.* 20 (2010) 6392–6407. doi:10.1039/b926348a.
- [22] T. Huang, W. Jiang, L. Duan, Recent progress in solution processable TADF materials for organic light-emitting diodes, *J. Mater. Chem. C* 6 (2018) 5577. doi:10.1039/c8tc01139g.
- [23] B.F. Zhang, K.G. Jespersen, C. Björström, M. Svensson, M.R. Andersson, V. Sundström, K. Magnusson, E. Moons, A. Yartsev, O. Inganäs, Influence of Solvent Mixing on the Morphology and Performance of Solar Cells Based on Polyfluorene Copolymer / Fullerene Blends, *Adv. Funct. Mater.* 16 (2006) 667–674. doi:10.1002/adfm.200500339.
- [24] T. Ye, S. Shao, J. Chen, L. Wang, D. Ma, Efficient Phosphorescent Polymer Yellow-Light-Emitting Diodes Based on Solution-Processed Small Molecular Electron Transporting Layer, *ACS Appl. Mater. Interfaces* 3 (2011) 410–416. doi:10.1021/am1010018.
- [25] O. Vybornyi, N.J. Findlay, P.J. Skabara, Scale-up Chemical Synthesis of Thermally-activated Delayed Fluorescence Emitters Based on the Dibenzothiophene-S,S-Dioxide Core, *JoVE*. (2017) e56501. doi:doi:10.3791/56501.
- [26] F.B. Dias, K.N. Bourdakos, V. Jankus, K.C. Moss, K.T. Kamtekar, V. Bhalla, J. Santos, M.R. Bryce, A.P. Monkman, Triplet harvesting with 100% efficiency by way of thermally activated delayed fluorescence in charge transfer OLED emitters, *Adv. Mater.* 25 (2013) 3707–3714. doi:10.1002/adma.201300753.
- [27] K. Norrman, A. Ghanbari-Siahkali, N.B. Larsen, Studies of spin-coated polymer films, *Annu. Reports Sect. "C."* 101 (2005) 174–201. doi:10.1039/b408857n.
- [28] D. Choi, B. Ahn, S.H. Kim, K. Hong, M. Ree, C.E. Park, High-Performance Triisopropylsilylethynyl Pentacene Transistors via Spin Coating with a Crystallization-Assisting Layer, *ACS Appl. Mater. Interfaces* 4 (2011) 117–122. doi:10.1021/am201074n.
- [29] B.T. Lee, T. Noh, H. Shin, O. Kwon, J. Park, B. Choi, M. Kim, D.W. Shin, Y. Kim, Characteristics of Solution-Processed Small-Molecule Organic Films and Light-Emitting Diodes Compared with their Vacuum-Deposited Counterparts, *Adv. Funct. Mater.* 19 (2009) 1625–1630. doi:10.1002/adfm.200801045.

- [30] K. Kumar, Sanat, K.E. Strawhecker, J.F. Douglas, A. Karim, The Critical Role of Solvent Evaporation on the Roughness of Spin-Cast Polymer Films, *Macromolecules*. 34 (2001) 4669–4672. doi:10.1021/ma001440d.
- [31] B.T. Chen, Investigation of the Solvent-Evaporation Effect on spin coating of Thin Films, *Polym. Eng. Sci.* 23 (1983) 399–403.
- [32] P. Xue, P. Wang, P. Chen, B. Yao, P. Gong, J. Sun, Z. Zhang, R. Lu, Chemical Science Bright persistent luminescence from pure organic molecules through a moderate intermolecular heavy atom effect †, *Chem. Sci.* 8 (2017) 6060–6065. doi:10.1039/C5SC03739E.
- [33] C. Yin, S. Ye, J. Zhao, M. Yi, L. Xie, Z. Lin, Y. Chang, F. Liu, H. Xu, N. Shi, Y. Qian, W. Huang, Hindrance-Functionalized π -Stacked Polymer Host Materials of the Cardo-Type Carbazole-Fluorene Hybrid for Solution-Processable Blue Electrophosphorescent Devices, *Macromolecules*. 44 (2011) 4589–4595. doi:10.1021/ma200624u.

Highlights

- Demonstrated the suitability of TADF exciplex DCz-DBTO2:TAPC for solution processable OLED emitter.
- Best results were achieved with chlorobenzene:chloroform solvent mixture with a 5:95 vol% ratio.
- EQE as high as $8.9 \pm 0.6\%$ were obtained which is comparable with the results previously published for the same TADF exciplex system for vacuum deposited devices.