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Toward highly efficient blue organic light-emitting diodes: fabricating a good-quality emissive layer cast from suitable solvents

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Spin-cast from various solvents, emissive layers show different film morphology and performance in solution-processed organic light-emitting diodes (OLEDs). Here we fabricated and demonstrated highly efficient blue OLEDs based on bis[3,5-difluoro-2-(2-pyridyl)phenyl]-(2-carboxypyridy)iridium(III) by choosing several kinds of solvents for spin-coating. Experiments indicate that the single-layer device with an emissive film cast from chlorobenzene shows best performance with a highest current efficiency of 18.99 cd/A, a maximum luminance of 20.5×10^3 cd/m^2 and an emission band centered at 474 nm. The efficiency achieved is the highest reported for solution-processed simple-manufactured OLEDs doped with transition metal phosphors emitting in the blue region.

Introduction

In the past several decades, organic light-emitting diodes (OLEDs) have attracted great deal of interest, which are expected as promising candidates for display and solid-state lighting applications.[1,2] Since C. W. Tang reported the first OLED based on thin films in 1987, amorphous organic functional films with smooth surface have been used in most OLEDs, which ensure the high uniformity and stability of devices under a high electric field.[3] As is known, the functional films in OLEDs are always prepared from two different methods, vacuum deposition and solution process, respectively. The former route is widely used to evaporate small molecules and allows for devices with multiple layers and even patterned structures by using shadow masks.[4] Whereas solution process is always used for OLEDs consisting of conjugated polymers[5-8] or ionic transition metal complexes[9-12], which are seldom thermally sublimable. Compared with vacuum deposition, solution process results in a much cheaper and simpler manufacture, which shows promise for producing larger-sized devices, such as screen printing[13-16] and ink jetting[17-19], but still have technical drawbacks. For example, solution-processed blend films exhibit large morphology variance depending on the processing conditions, which greatly determines the device performance such as electroluminescent spectra.[20] However, researches on spin-coating solvent dependence of device efficiencies are still scarce,[21] although significance of fundamental understanding of the functional films in devices has been increased along with the continuous progress of OLEDs.[22,23]

On the other hand, the application of blue OLEDs is always limited by low efficiencies. Since reported in 2003, the neutral cyclometalated iridium complex, bis[3,5-difluoro-2-(2-pyridyl)phenyl]-(2-carboxypyridy)iridium(III) (sometimes also called bis(4,6-difluorophenylpyridinato)-picolinate, FIrpic for short) has been widely used as a phosphor in blue OLEDs.[24] Efforts have focused on how to improve the performance of devices based on FIrpic, such as developing novel molecules as hosts,[25-29] electron-transport[30] or carrier-charge blocking[31] materials and even employing multilayer structures[32].

Here we fabricated and demonstrated highly efficient solution-processed single-layer blue OLEDs based on FIrpic with good-quality emissive layers cast from 1,2-dichloroethane, chlorobenzene and 1,2-dichlorobenzene, respectively. Finally the device with an emissive layer cast from chlorobenzene shows the highest efficiency of 18.99 cd/A and a maximum luminance up to 20.5×10^3 cd/m^2.

Results and discussion

In this article, solution-processed single-layer OLEDs were fabricated with a following structure: ITO/ PEDOT: PSS (60 nm)/ PVK: OXD-7: 10 *wt.* % FIrpic (x mg/mL)/ Cs_2CO_3 (y nm)/ Al (150 nm), as depicted in **Scheme 1**. A range of solvents with increasing boiling points from 1,2-dichloroethane, chlorobenzene to 1,2-dichlorobenzene were selected to prepare the light-emitting solutions. Here Poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT: PSS) serves as a hole-injection layer, PVK is poly(N-vinylcarbazole)

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as the host, OXD-7 is 1,3-bis(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)benzene as the electron transport material, and FIrpic is the blue dopant, energy level diagram of which is also shown in **Scheme 1**. Total concentration of the emissive solution and thickness of the cesium carbonate (Cs_2CO_3) layer were varied to optimize the device performance. During fabrication of devices, first the glass substrate was precoated with an about 100 nm thick layer of indium-tin oxide (ITO) with a sheet resistance of about 20 Ω per sq, then cleaned by exposure to oxygen plasma and UV-ozone ambient, and finally used for devices. PEDOT: PSS layer was spin-coated in air at 3000 rpm, cast from deionized water and then baked at 200 °C for 10 min, yielding an approximate 60 nm-smooth film. Next the light-emitting layer was spin-coated at 1500 rpm in a glove box filled with nitrogen, then annealed at 80 °C for 30 min. Subsequently, the sample was transferred into a vacuum chamber with a low pressure of $2\text{-}5\times10^{-4}$ Pa, where Cs_2CO_3 as the electron injection layer and aluminium (Al) as the cathode were evaporated at rates of 0.2 and 5 Å/s, respectively.

<Scheme 1>

Performance of single-layer OLEDs with the light-emitting layers cast from 1,2-dichloroethane with different total solution concentrations are depicted in **Figure 1** and **Table 1**. For these devices, thickness of the Cs_2CO_3 layer was fixed at 2.3 nm. **Figure 1(a)** and **(b)** show the current density (*J*) and luminance (*L*) *versus* voltage (*V*) characteristics of devices, respectively. As shown in **Table 1**, *J* (5 mg/mL) at 18 V exceeds 11667 A/m^2, much higher than *J* (10 mg/mL) (2255 A/m^2) and *J* (15 mg/mL) (2294 A/m^2). And the current efficiency of the device cast from 5 mg/mL light-emitting solution is only 0.58 cd/A, quite lower than devices cast from the 10 mg/mL and 15 mg/mL light-emitting solutions. It can be explained that the total concentration of 5 mg/mL is too dilute for spin-coating, leading to a quite thin film with a low electrical resistance. We obtained the highest current efficiency of 14.67 cd/A at the total concentration of 10 mg/mL. In addition, all the devices with different total concentrations emit blue, and the electroluminescent spectra are quite similar, centered at 474 nm (see **Figure 1(c)** and **Table 1**).

<Figure 1>

<Table 1>

Figure 2 and **Table 2** show performance of OLEDs with the emissive layers cast from chlorobenzene with varied total solution concentrations. The thickness of the Cs_2CO_3 layer was also 2.3 nm. *J-L-V* curves shift towards the high voltages as the total concentrations of solutions increase. *J* (10 mg/mL) at 18 V also exceeds 11667 A/m^2, while *J* (20 mg/mL) is only 2842 A/m^2, but still much higher than *J* (30 mg/mL) (100.2 A/m^2). It suggests that as the concentrations of solution increase, the light-emitting film turns thicker, leading to a decreased current. Accordingly, turn-on voltages of the devices also show a sharp increase along with the increasing total concentrations. At the total concentration of 20 mg/mL, we attained a high current efficiency of 15.84 cd/A and a maximum luminance of 20.72×10^3 cd/m^2, even higher than that of the device cast from 1,2-dichloroethane.

<Figure 2>

<Table 2>

Next we chose 1,2-dichlorobenzene as the spin-coating solvent and observed a clearer phenomenon. As shown in **Figure 3** and **Table 3**, *J* (30 mg/mL) at 18 V is 2301 A/m^2, quite higher than *J* (40 mg/mL) (434 A/m^2), while *J* (50 mg/mL) decreases sharply to only 10.9 A/m^2. At the total concentration of 40 mg/mL, the best device performance was achieved with a current efficiency of 12.51 cd/A and a maximum luminance of 10.71×10^3 cd/m^2, however, not so good as that of the device cast from chlorobenzene.

<Figure 3>

<Table 3>

To further investigate the effect of solvent condition on the morphology behaviour, atomic force microscopy (AFM, SPA-400) measurement was carried out for the emissive films cast from different solvents. Seen from **Table S1** in **Supplementary Information**, the surface tension of 1,2-dichloroethane, chlorobenzene and 1,2-dichlorobenzene is 31.7, 32.5 and 36.2 mN/m, increasing along with the raised boiling points, 83.5, 132.2 and 180.4 ^{o}C, respectively. As depicted in **Figure 4**, surface roughness of the film cast from 1,2-dichlorobenzene is only 0.50 nm, lower than that of the film cast from chlorobenzene (0.56 nm) and 1,2-dichloroethane (0.74 nm). It is because 1,2-dichlorobenzene has a higher surface tension than 1,2-dichloroethane and chlorobenzene, which retards volatilization of the solvents and helps forming smooth and compacted amorphous films. And peak-valley values of the film cast from 1,2-dichloroethane and 1,2-dichlorobenzene both approach 14 nm, much higher than that of the film cast from chlorobenzene (8.88 nm). Taken together, the film cast from chlorobenzene shows best morphology behaviour, which enables solution-processed OLEDs with highest efficiency.

<Figure 4>

Furthermore, thickness of the Cs_2CO_3 electron injection layer was also varied to optimize the device performance, as depicted in **Table 4**, **Figure S1-3** and **Table S2-4**. For devices cast from 1,2-dichloroethane, the total concentration of light-emitting solution was fixed at 10 mg/mL and we gained a high current efficiency of 14.67 cd/A at the 2.3 nm Cs_2CO_3 layer. For devices cast from chlorobenzene with the total concentration of 20 mg/mL, a highest current efficiency of 18.99 cd/A was attained at the 2.6 nm Cs_2CO_3 layer. And for devices cast from 1,2-dichlorobenzene, when the Cs_2CO_3 layer was 2.0 nm and total concentration was 40 mg/mL, the current efficiency reached 12.58 cd/A.

<Table 4>

Conclusions

In summary, emissive layers for solution-processed single-layer OLEDs were prepared from solvents with various surface tension, 1,2-dichloroethance, chlorobenzene and 1,2-dichlorobenzene, respectively, resulting in varied morphology. Then device fabrication was completed on evaporation of the Cs_2CO_3/ Al cathode. According to the experimental results, the emissive layer spin-cast from chlorobenzene shows a best surface morphology with the highest current efficiency of

18.99 cd/A and a maximum luminance of 20.50×10^3 cd/m^2, among the highest reported for analogous solution-processed blue OLEDs. Our work suggests suitable solvents for spin-coating, in order to improve performance of solution-processed OLEDs. In addition, deeper understanding of molecule stacking and orientation in the corresponding films would be our further work.

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Notes and references

‡ Experimental: In this article, all the reactants and solvents mentioned were purchased from commercial sources and used as received unless otherwise stated. The current-voltage-brightness characteristics of devices were measured with Keithley 4200 semiconductor system in ambient atmosphere without further encapsulations. The electroluminescent spectra were then collected with a Photo Research PR705 spectrophotometer.

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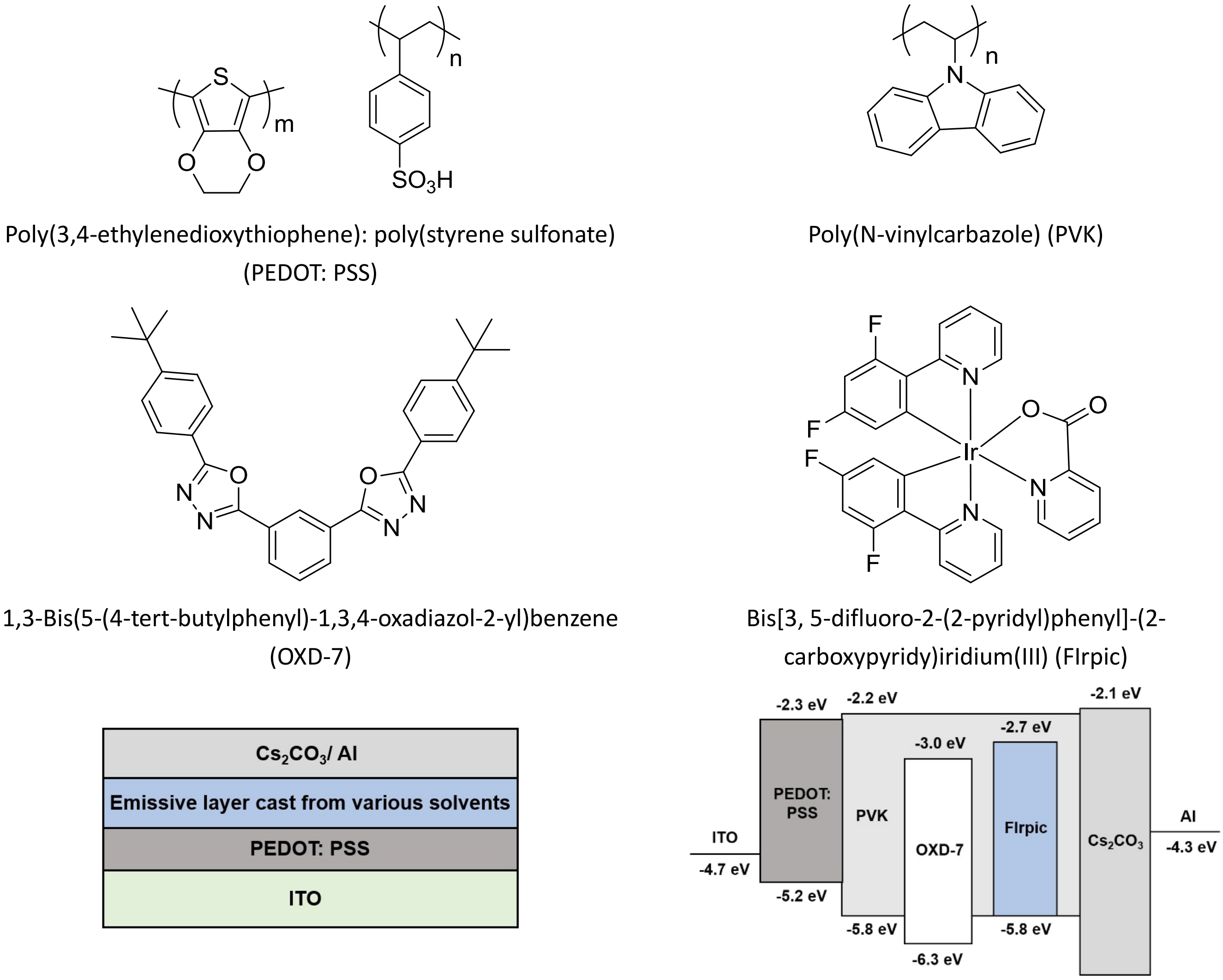
Scheme 1. Chemical structures, energy level diagram of materials and device structure for single-layer OLEDs.



Poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT: PSS)

Poly(N-vinylcarbazole) (PVK)

1,3-Bis(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)benzene (OXD-7)

Bis[3, 5-difluoro-2-(2-pyridyl)phenyl]-(2-carboxypyridy)iridium(III) (FIrpic)

Figure 1. Performance of solution-processed OLEDs with the emissive layers cast from 1,2-dichloroethane with different total solution concentrations. The structure of OLED is ITO/ PEDOT: PSS (60 nm)/ PVK: OXD-7: 10 *wt.* % FIrpic (*x* mg/mL)/ Cs_2CO_3 (2.3 nm)/ Al (150 nm), *x* = 5, 10 or 15. **(a)** *J* (current density) *versus V* (voltage) characteristics, **(b)** *L* (luminance) *versus V* (voltage) characteristics and **(c)** electroluminescent spectra of OLEDs.

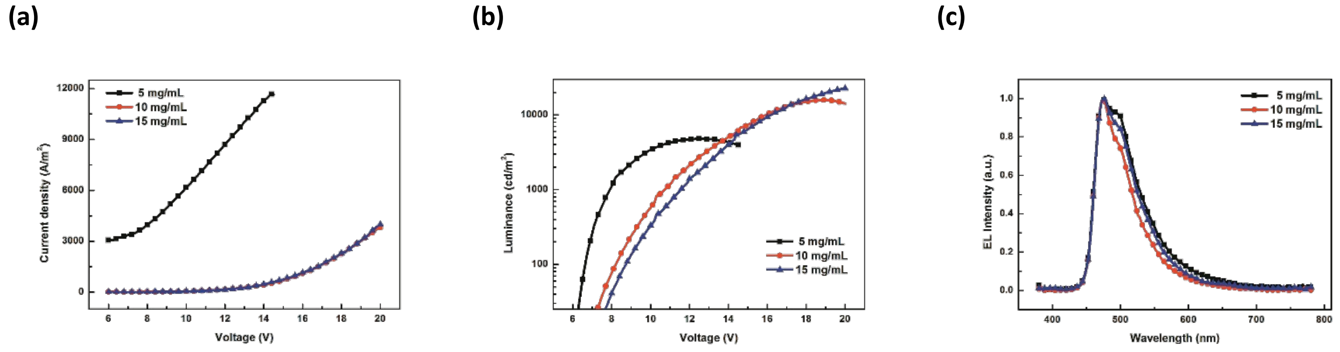


Figure 2. Performance of solution-processed OLEDs with the emissive layers cast from chlorobenzene with different solution concentrations. The structure of OLED is ITO/ PEDOT: PSS (60 nm)/ PVK: OXD-7: 10 *wt.* % FIrpic (*x* mg/mL)/ Cs_2CO_3 (2.3 nm)/ Al (150 nm), *x* = 10, 20 or 30. **(a)** *J* (current density) *versus V* (voltage) characteristics, **(b)** *L* (luminance) *versus V* (voltage) characteristics and **(c)** electroluminescent spectra of OLEDs.

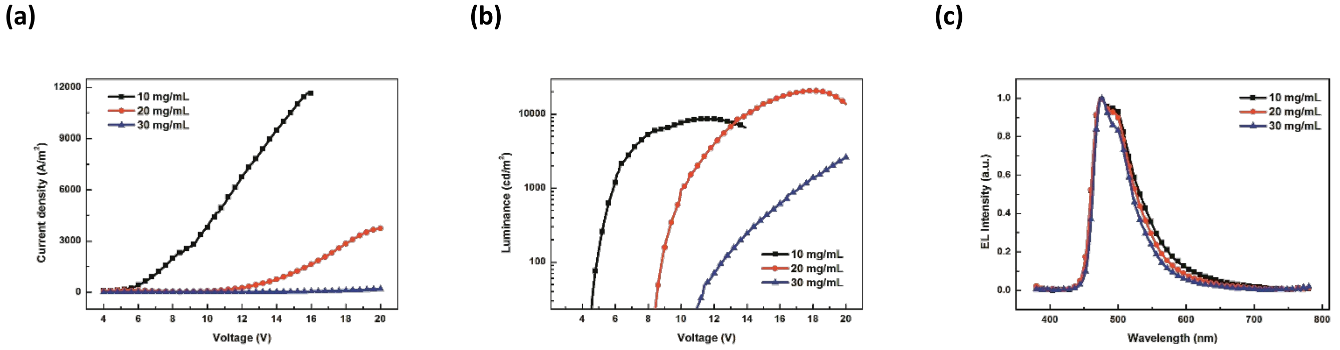


Figure 3. Performance of solution-processed OLEDs with the emissive layers cast from 1, 2-dichlorobenzene with different solution concentrations. The structure of OLED is ITO/ PEDOT: PSS (60 nm)/ PVK: OXD-7: 10 *wt.* % FIrpic (*x* mg/mL)/ Cs_2CO_3 (2.3 nm)/ Al (150 nm), *x* = 30, 40 or 50. **(a)** *J* (current density) *versus V* (voltage) characteristics, **(b)** *L* (luminance) *versus V* (voltage) characteristics and **(c)** electroluminescent spectra of OLEDs.

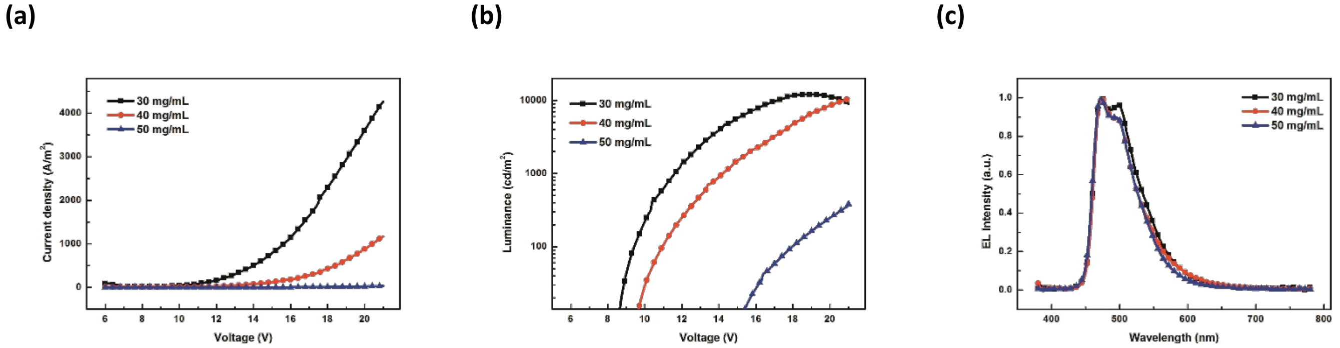
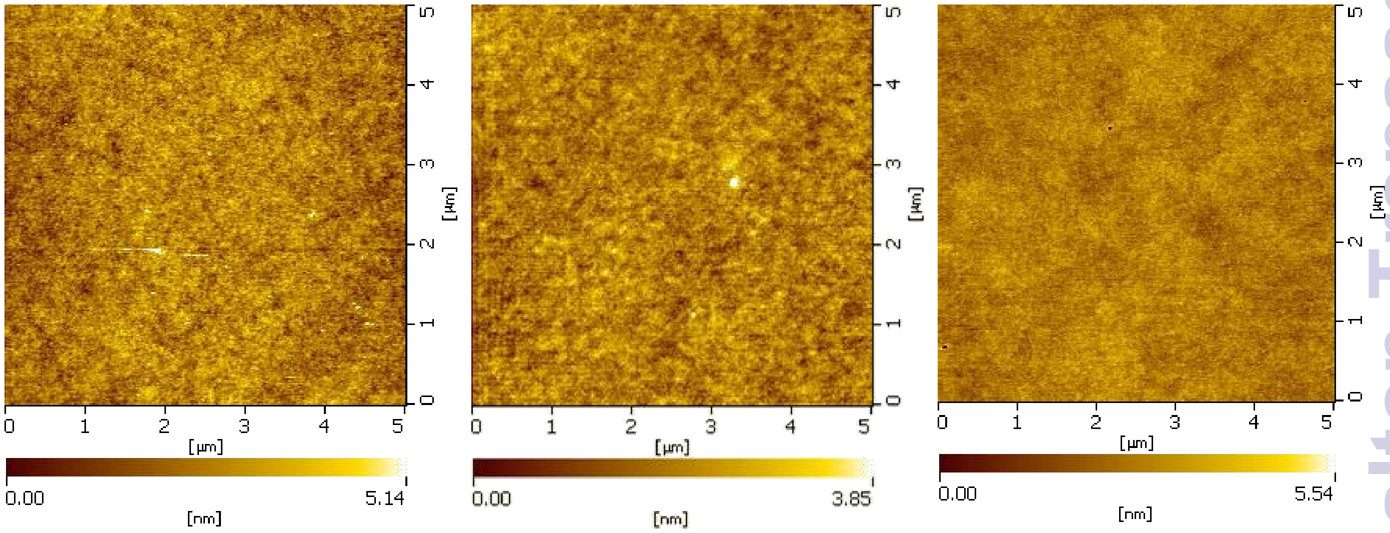


Figure 4. Surface morphology of the emissive layers cast from various solvents in optimized devices. (a) 1,2-dichloroethane, **(b)** chlorobenzene and **(c)** 1,2-dichlorobenzene. Here *PV* is the peak-valley value and *RMS* is root mean square.



(a) *PV* = 13.97 nm, *RMS* = 0.74 nm **(b)** *PV* = 8.88 nm, *RMS* = 0.56 nm **(c)** *PV* = 13.82 nm, *RMS* = 0.50 nm

Table 1. Detailed performance of solution-processed OLEDs with the emissive layers cast from 1,2-dichloroethane with different solution concentrations. The structure of OLED is ITO/ PEDOT: PSS (60 nm)/ PVK: OXD-7: 10 *wt.* % FIrpic (*x* mg/mL)/ Cs_2CO_3 (2.3 nm)/ Al (150 nm), *x* = 5, 10 or 15.

x	Turn-on Voltage	Current Efficiency	Luminance	Current Density	Wavelength	CIE
	V_{on} [V]	η_{max} [cd/A]	L_{max} [cd/m^2]	J [A/m^2] at 18 V	λ [nm]	(*x*, *y*)
5	6.1	0.58	4.77×10^3	>11667	474	(0.20, 0.38)
10	6.5	14.67	15.81×10^3	2255	474	(0.17, 0.34)
15	6.8	9.35	24.18×10^3	2294	474	(0.18, 0.37)

Table 2. Detailed performance of solution-processed OLEDs with the emissive layers cast from chlorobenzene with different solution concentrations. The structure of OLED is ITO/ PEDOT: PSS (60 nm)/ PVK: OXD-7: 10 *wt.* % FIrpic (*x* mg/mL)/ Cs_2CO_3 (2.3 nm)/ Al (150 nm), *x* = 10, 20 or 30.

x	Turn-on Voltage	Current Efficiency	Luminance	Current Density	Wavelength	CIE
	V_{on} [V]	η_{max} [cd/A]	L_{max} [cd/m^2]	J [A/m^2] at 18 V	λ [nm]	(*x*, *y*)
10	4.4	3.65	8.67×10^3	>11667	474	(0.20, 0.38)
20	8.2	15.84	20.72×10^3	2842	474	(0.18, 0.36)
30	10.1	14.21	3.66×10^3	100.2	474	(0.17, 0.36)

Table 3. Detailed performance of solution-processed OLEDs with the emissive layers cast from 1, 2-dichlorobenzene with different solution concentrations. The structure of OLED is ITO/ PEDOT: PSS (60 nm)/ PVK: OXD-7: 10 *wt.* % FIrpic (*x* mg/mL)/ Cs_2CO_3 (2.3 nm)/ Al (150 nm), *x* = 30, 40 or 50.

x	Turn-on Voltage	Current Efficiency	Luminance	Current Density	Wavelength	CIE
	V_{on} [V]	η_{max} [cd/A]	L_{max} [cd/m^2]	J [A/m^2] at 18 V	λ [nm]	(*x*, *y*)
30	8.5	8.36	12.14×10^3	2301	474	(0.18, 0.39)
40	9.3	12.51	10.71×10^3	434	474	(0.18, 0.37)
50	14.6	12.37	383	10.9	472	(0.16 0.35)

Table 4. Detailed performance of optimized solution-processed OLEDs with the emissive layers cast from various solvents. For device I, the emissive layer was cast from 1,2-dichloroethane with a structure of ITO/ PEDOT: PSS (60 nm)/ PVK: OXD-7: 10 *wt.* % FIrpic (10 mg/mL) / Cs_2CO_3 (2.3 nm)/ Al (150 nm). For device II, the emissive layer was cast from chlorobenzene with a structure of ITO/ PEDOT: PSS (60 nm)/ PVK: OXD-7: 10 *wt.* % FIrpic (20 mg/mL) / Cs_2CO_3 (2.6 nm)/ Al (150 nm). For device III, the emissive layer was cast from 1,2-dichlorobenzene with a structure of ITO/ PEDOT: PSS (60 nm)/ PVK: OXD-7: 10 *wt.* % FIrpic (40 mg/mL) / Cs_2CO_3 (2.0 nm)/ Al (150 nm).

Device	Turn-on Voltage	Current Efficiency	Luminance	Current Density	Wavelength	CIE
	V_{on} [V]	η_{max} [cd/A]	L_{max} [cd/m^2]	J [A/m^2] at 18 V	λ [nm]	(*x*, *y*)
I	6.5	14.67	15.81×10^3	2255	474	(0.17, 0.34)
II	8.4	18.99	20.50×10^3	1346	474	(0.16, 0.34)
III	9.1	12.58	5.75×10^3	185	478	(0.18, 0.40)

Cast from chlorobenzene, the light-emitting layer shows best morphology and a highest efficiency of 18.99 cd/A in single-layer FIrpic-based OLEDs.

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