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Unmodified small-molecule organic light-emitting diodes by blade coating

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ABSTRACT

Blade coating with substrate heating and hot wind is demonstrated to be a general platform for multi-layer deposition of unmodified small-molecule organic semiconductors. Most unmodified small molecules, originally designed for vacuum evaporation, can be blade coated while the solubility is above 0.5 wt.%. High uniformity is achieved for scale over 5 cm. Orange devices by evaporation and blade coating are compared with 4,4'-bis(carbazol-9-yl)biphenyl (CBP) as the host, iridium(III) bis(4-(4-*t*-butylphenyl)thieno[3,2-*c*]pyridinato-*N,C*^{2'})acetylacetonate (PO-01-TB) as the emitter. The efficiency difference is within 10%. When 2,6-bis(3-(9H-carbazol-9-yl)phenyl)pyridine (26DCzPPy) is used as the host, the current efficiencies are 40 cd/A for orange, 32 cd/A for green, and 20 cd/A for blue. The optimized organic light-emitting diodes (OLED) structure developed for vacuum deposition can therefore be exactly copied by the low cost blade coating method in solution.

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1. Introduction

In the past 20 years organic light-emitting diodes (OLEDs) based on small molecules evaporated in vacuum have shown continuously improving efficiency, and is now a promising technology for solid-state lighting and display. The performance of vacuum processed OLED with multi-layer structures for charge balance and low driving voltage suppresses the solution-processed OLED usually involving conjugated polymers. In addition to the optimized multi-layer structure, compared with polymers the small molecules have the advantages of higher purity, more flexible molecular design, and absence of variation due to molecular weight distribution. In order to reduce the high

cost of large-area vacuum deposition, there is a growing effort to fabricate small molecule OLED by solution process. Chemical modifications of the molecules are usually necessary. For example cross-linking groups can be added to reduce the inter-layer dissolution [1], and side groups to enhance the solubility [2]. Unfortunately the modified small molecules usually have altered electronic structure, resulting in different carrier transport or luminescence properties. Consequently even if the similar multi-layer structure can be made by such modified small molecules, the originally optimized device performance is lost. So far the vacuum deposited OLED in general still has superior performance than the solution processed OLED based on either polymers or modified small molecules. There is therefore a dilemma between efficiency and cost. Such dilemma can be removed only if there exists a general platform to fabricate by solution the optimized vacuum-deposited OLED structure with exactly the same materials.

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In this work we show that a blade coating method with rapid drying satisfies all the requirements for such a general platform for solution deposition of unmodified small molecules with multi-layer structures. The difficulties of solution deposition of unmodified small molecules, i.e. the ones originally designed for vacuum deposition, include poor solubility and poor film-forming ability due to weak inter-molecular interaction. Indeed for conventional spin coating many small molecules do not form uniform connected film even if they can be dissolved. Blade coating was previously applied to OLED multi-layer structures of polymers and modified small molecules with high solubility and enhanced inter-molecular interaction [3,4]. By the introduction of rapid drying through heating from the substrate and hot wind from the top, multi-layer structures can be made for unmodified small molecules with poor solubility and poor film-forming ability. The rapid drying prevents the inter-layer dissolution. Cylindrical bar has been used for coating of organic semiconductor layer. However the wires on the bar may damages the underlying layer [5], and the lack of rapid drying makes multilayer impossible due to dissolution [6]. Furthermore, the absence of the centrifugal force during drying prevents the unpredictable distribution and poor uniformity of the small molecules as in the case of spin coating.

Using blade coating multi-layer orange, green, and blue OLED are made entirely of unmodified small molecules, with commonly used hole transport, electron transport, emission layer host, as well as phosphorescent emitters. Exactly the same device structure is made by both vacuum deposition and blade coating and then compared. The efficiency turns out to be close. 40 cd/A is achieved for orange, 33 cd/A for green, and 20 cd/A for blue emission. Almost all small molecules can be blade coated if the solubility is above a mere 0.5 wt.% in some solvent. If the solubility is below 0.5 wt.% the film thickness will be too low. Heating of the solution usually enhances the solubility but the organic materials may precipitate during blade coating as temperature drops and poor uniformity results. Blade coating is therefore able to realize the exact optimized vacuum-deposited OLED structure by solution process without any chemical modification. There is no need to redesign the materials and device structures. Such fabrication platform solves the long dilemma of performance and cost for OLED.

2. Experimental

Blade coating is done using a blade with gap of 30–120 μm to the substrate. The solution of 30–40 μl is delivered in front of the blade by a pipette, the blade is then moved by hand at about 40 cm/s to cover the active area of the device by the wet film. Rapid drying is crucial for multi-layer deposition and large-area uniformity. Hot plate heating from the bottom and hot wind from above are simultaneously applied to achieve drying in 1 s. Note that hot plate alone is insufficient. When the temperature is low, the solvent of the second layer is not expelled quickly enough before dissolution of the first layer happens. When the temperature is high the first layer is softened and easily dissolved. Hot wind removes the solvent efficiently without significantly softening the previous layer. Hot wind is also

necessary to ensure large-area uniformity by inhibiting re-flow during drying. In practice the hot plate is at 60–80 $^{\circ}\text{C}$ for rapid drying. Hot wind around 70 $^{\circ}\text{C}$ from a hair dryer is applied. Dry films forms before dissolution could happen. The blade coating procedure is shown in Fig. 1.

For device fabrication conditions we start with the orange device structure ITO/PEDOT:PSS (50 nm)/NPB (40 nm)/CBP:PO-01-TB = 94:6 (30 nm)/TPBI (30 nm)/LiF (0.8 nm)/Al (100 nm). The indium-tin-oxide (ITO) glass is cleaned by standard procedure. 50 nm layer of poly-(3,4-ethylenedioxythiophene) doped with poly-(styrenesulfonate) (PEDOT:PSS, CLEVIOS™ P VP Al4083) is spin coated at 2000 rpm on the ITO glass, then annealed at 200 $^{\circ}\text{C}$ for 15 min in air. N,N'-bis(Naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (NPB) is dissolved in toluene with 0.5 wt.%. For simplicity and lack of dissolution problem on PEDOT:PSS, the blade coating is not done on hot plate but on a spinner for the hole transport layer (HTL) of NPB. The hole transport layer can also be blade coated on hot plate with hot wind for the same device performance. The film is annealed at 120 $^{\circ}\text{C}$ for 5 min. The emission layer (EML) is a blend of 4,4'-bis(carbazol-9-yl)biphenyl (CBP) and iridium(III) bis(4-(4-*t*-butylphenyl)thieno[3,2-*c*]pyridinato-*N,C'*)acetylacetonate (PO-01-TB) [7] in the weight ratio of 94:6. The blend in chloroform with 0.5 wt.% is blade coated with 60 μm blade gap and 30 μl of solution delivered by pipette on hot-plate at 60 $^{\circ}\text{C}$, resulting in 30 nm solid film, then annealed at 80 $^{\circ}\text{C}$ for 10 min in vacuum. The electron transport layer (ETL, 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBI) of 30 nm is blade coated with hot plate temperature of 80 $^{\circ}\text{C}$, blade gap of 60 μm , 40 μl of 0.5 wt.% methanol solution. LiF

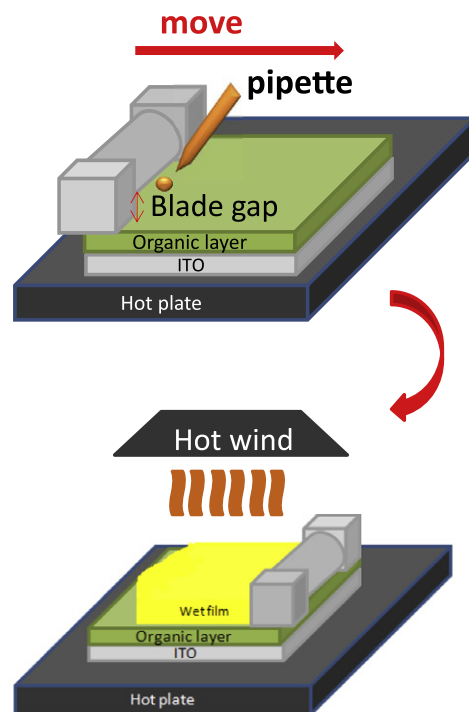


Fig. 1. The blade-only process.

and Al are evaporated in vacuum. The active area is 4 mm². For orange devices with CBP host and other HTL, the fabrication conditions are the same except for the HTL. 4,4',4''-Tris(carbazol-9-yl)triphenylamine (TCTA) is dissolved in toluene at 1 wt.% then blade coated with gap of 60 μm followed by spinning at 3000 rpm. Di-[4-(N,N-ditolylamino)-phenyl]cyclohexane (TAPC) is dissolved in toluene at 0.5 wt.% then blade coated with gap of 60 μm followed by spinning at 1000 rpm. Both of these two films are annealed in vacuum at 120 °C for 10 min, resulting in thickness of 40 nm. For orange devices with 2,6-bis(3-(9H-carbazol-9-yl)phenyl)pyridine (26DCzPPy) as the host, all conditions are the same with the former one. For green devices with tris[2-(p-tolyl)pyridine]iridium(III) (Ir(mppy)₃) as the emitter and CBP and 26DCzPPy as the host, the fabrication is the same as the orange device except for the EML. The blend in chloroform with 0.5 wt.% is blade coated with 60 μm gap and 40 μl of solution delivered by pipette on hot-plate at 60 °C, resulting in 40 nm solid film. The EML film is then annealed at 80 °C for 10 min in vacuum. For the blue device with bis(3,5-difluoro-2-(2-pyridyl)phenyl)-(2-carboxypyridyl)iridium(III) (Flrpic) emitter, the EML is deposited by chlorobenzene solution. The blend in chlorobenzene with 1.6 wt.% is blade coated with 60 μm gap and 20 μl of solution

delivered by pipette on hot plate at 80 °C, resulting in 60 nm solid film. The EML film is then annealed at 80 °C for 10 min in N₂. The molecular structures of the compounds used in this study are shown in Fig. 2.

3. Results and discussion

The major challenge of all solution process of multi-layer deposition is that the solvent of the second layer may dissolve the first dry layer. The absence of dissolution and a sharp bi-layer structure of blade coating are verified from several independent perspectives. First, a region of the first layer is removed by an acetone-immersed cotton stick. The edge of the region is then inspected after the second layer is blade coated and dried. If the first layer was dissolved the edge would disappear or at least blurred. The standard condition A of substrate temperature of 60 °C by hot plate heating with hot wind is compared with a condition B with reduced substrate temperature of 30 °C and without hot wind for NPB beneath CBP:PO-01-TB. As shown in Fig. 3(a) the edge remains sharp for condition A with rapid drying while it is blurred in condition B with delayed drying. The height profiles across the edge are also shown in Fig. 3(b). The profile is smooth in condition A,

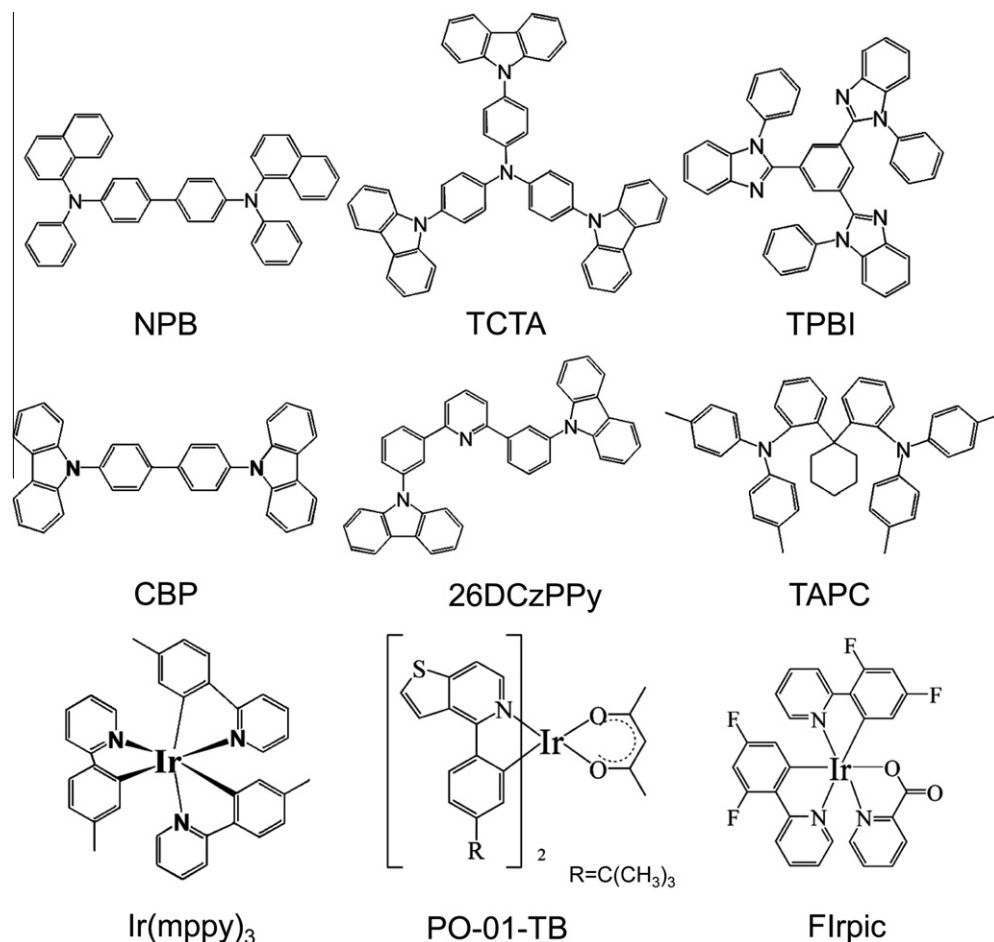


Fig. 2. The molecule structures of the compounds used in this study.

while it is irregular and expanded in condition B due to dissolution of the first layer. Second the total thickness of the film inside and outside the region after coating of the second layer can be measured. The results for NPB and CBP:PO-01-TB bi-layer with a square region in removed are labeled in Fig. 3(c). The expected thicknesses are 15 nm and 33 nm for first and second layer if they are blade coated alone on PEDOT:PSS. Indeed outside the region it is the sum of the thicknesses of the two layers, while inside the region it is the thickness of the second layer. Third the bi-layer structure can be verified by the absence of the emission from the first hole transport layer in devices. The hole transport layer blocks the electrons and no recombination takes place there with a sharp interface. However if the layers are mixed there will be blue emission from the hole transport molecules. In Fig. 4(a) the OLED emission spectra for the devices with NPB as the hole transport layer and CBP doped with PO-01-TB as the emission layer are compared for the cases with chloroform and toluene solution. To completely prevent dissolution the hot plate and hot wind conditions need to be adjusted for each solvent. For this particular condition toluene has partial dissolution because of the slower drying compared with chloroform. Blue emission from NPB appears only for toluene solution, indicating that a sharp interface exists between NPB and CBP:PO-01-TB layers with chloroform solution. Finally the scanning electron microscope (SEM) image for the cross section is shown in

Fig. 4(b) to demonstrate the smoothness of the multi-layer film in the nanometer scale. The interface is invisible in SEM because the atomic compositions of the two layers are similar. The total thickness is the sum of the two layers individually coated as marked in Fig. 4(b). Due to the roughness of the surface of layers, there is a error range of thickness between 2 and 3 nm at each layer. Therefore we aim to make the combination of these two layers with the error range fewer than 5 nm.

In addition to prevent dissolution in multi-layer structure, the rapid drying blade coating yield highly uniform film in large area for small molecules with low solubility and without intermolecular entanglement shown in Fig. 4(c). For area up to 4 cm by 4 cm the variation of film thickness is below 5 nm for an mean value of 50 nm. Such uniformity is impossible for spin coating for many small molecules. For example the result for spin coating of NPB in 0.5 wt.% of toluene solution gives disconnected film shown in Fig. 5(a) because of the lack of strong interactions among the molecules. On the other hand blade coating is successful for NPB originally designed for vacuum evaporation shown in Fig. 5(b). The blue color appears due to the NPB films are lighted by UV lamp.

The structure for orange phosphorescent OLED is shown in Fig. 6(a) with common HTL of NPB, ETL of TPBI, and EML host of CBP. The orange emitter is PO-01-TB. The ionization potential for the highest occupied molecular orbital (HOMO) and electron affinity for the lowest unoccupied

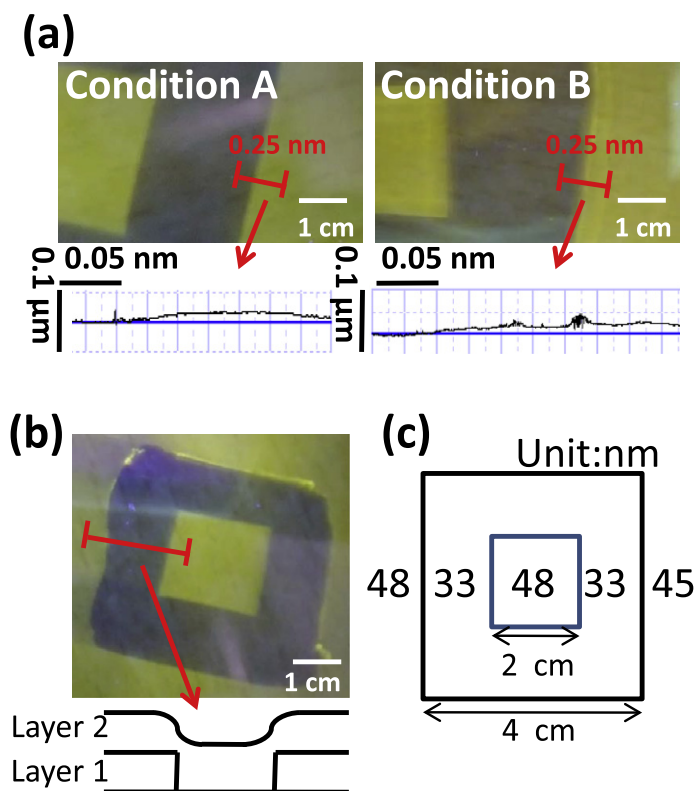


Fig. 3. (a) The images of deposition condition A and B, (b) The picture and the profile of condition A and (c) The thicknesses distribution of condition A. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

molecular orbital (LUMO) levels are labeled in eV. The host to emitter weight ratio is 94:6. Each layer can be either blade coated or vacuum evaporated. The surface morphology for the emission layers are shown in Fig. 5(c) and (d) with a remarkable difference. The lower roughness and absence of aggregates in blade coating implies that potentially it has a better stability. The tri-layer device structure is realized by blade coating or evaporation in four different combinations E/E, B/B, B/E, and E/B. E or B represents evaporation or blade for the HTL/EML bi-layer and ETL. For example E/E means the entire device is vacuum deposited and B/E means HTL/EML are blade coated and ETL is evaporated. The device characteristics are shown in Fig. 6(b). The highest current efficiency for E/E and B/E devices are both about 40 cd/A, indicating that the difference in emissive layer morphology does not affect the efficiency much. The efficiency is 37 cd/A for B/B device demonstrating approximately no difference with vacuum deposition devices. Considering the great reduction in fabrication cost such small difference in efficiency is not a major problem. High-performance small molecule OLED structure originally designed for vacuum deposition is therefore proved to be possibly made entirely by solution deposition. The E/B device shows a relatively high driving voltage probably also due to higher TPBI thickness which is tuned by coating on PEDOT:PSS. The high roughness of evaporated EML may lead to thicker wet film during blade motion.

In Fig. 7 CBP is replaced by the host 26DCzPPy which is a bipolar transport host by balanced electron and hole mobility [8]. The maximal current efficiency of 30 cd/A is close to CBP host. One advantage of 26DCzPPy over CBP is its lower device variations presumably due to the higher molecular weight and less tendency for crystallization. For the host of 26DCzPPy, three common hole transport materials NPB, TAPC, and TCTA are compared. The HOMO levels are 5.3, 5.5, and 5.7 eV below vacuum respectively, whereas the LUMO levels are 2.4, 2.0, and 2.3 eV respectively. As shown in Fig. 7 the device with TAPC has the highest current efficiency of 40 cd/A, corresponding to 13% of external quantum efficiency, probably due to the highest electron blocking barrier. The power efficiency is 20 lm/W at 1000 cd/m², which is close to the result of the all-evaporated devices. The power efficiency is shown in Fig. 7. The results are also similar to vacuum deposited OLED with other orange emitter in CBP host [9]. Devices with NPB shows the lowest turn-on voltage about 3 V probably due to the lowest hole injection barrier from PEDOT:PSS anode into the hole transport layer. Holes may transport through the PO-01-TB emitters so the high barrier between NPB and the 26DCzPPy HOMO level does not cause high operation voltage.

Now we turn to green phosphorescent devices with Ir(mppy)₃ emitter and TCTA hole transport layer. Both CBP and 26DCzPPy are used as the emission layer host, with host to emitter weight ratio of 94:6. The device structure is the same as the orange device above except for the optimal thickness. As shown in Fig. 8(a) and (b) both hosts give maximal efficiency about 30–35 cd/A, whereas 26DCzPPy has less variation similar to the case of orange devices. The thickness of TCTA, EML, and TPBI is 30, 40, and 40 nm, respectively. The current efficiency is close to

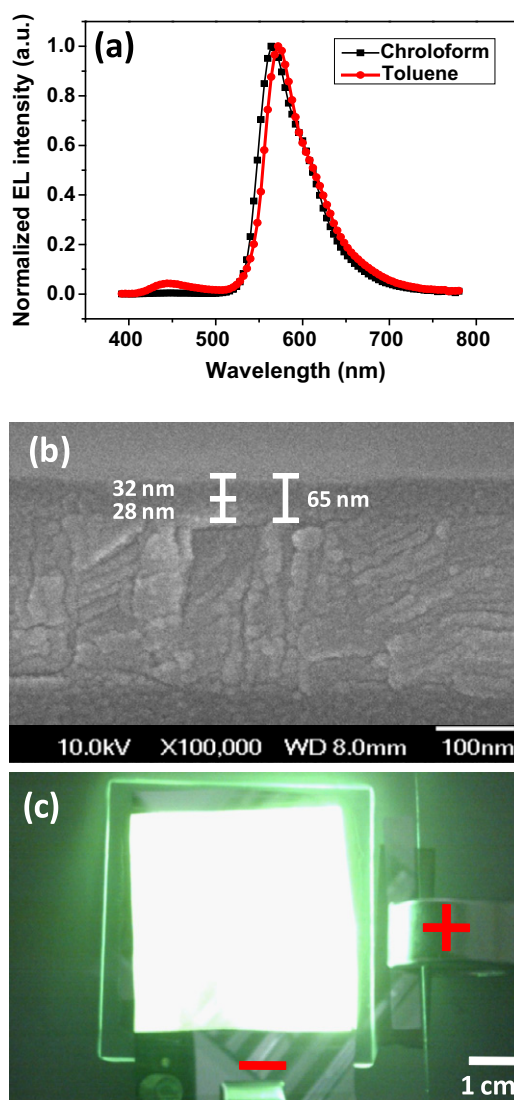


Fig. 4. (a) The OLED emission spectra are the orange devices using different conditions of emission layer, (b) The SEM image of bi-layer structure, (c) The images of highly uniform green device with 4 cm by 4 cm active area.

the values obtained in vacuum deposited green OLED with CBP host and TPBI ETL [10,11]. Even though there is some difference in the hole transport material and layer thicknesses, the similarity between the efficiencies for blade coated and evaporated green devices implies that unmodified green OLED structure can be realized by solution process without significant reduction in performance. Similar device performance is obtained when the weight ratio of the emitter is varied in the range of 6% up to 18%. This indicates that uniform emitter dispersion in the host is achieved in blade coating even for very high emitter concentration. The efficiency would drop greatly if the emitter molecules form aggregates due to self-quenching.

In addition to TCTA above, TAPC is also used as the hole transport material for the green devices. The device characteristics for TAPC with various thickness is shown in

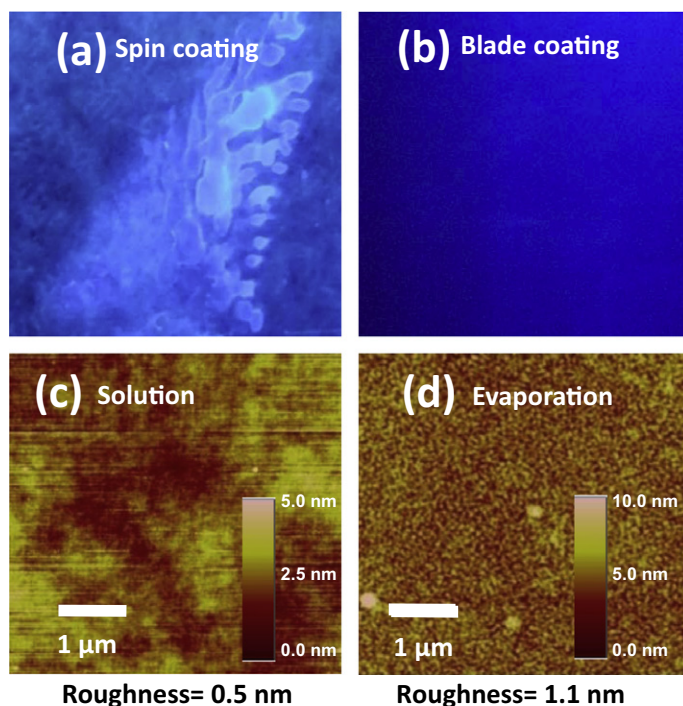


Fig. 5. The films of NPB are resulted by (a) spin coating and (b) blade coating, (c) AFM images of emission layer made by spin coating process and (d) vacuum deposition process. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

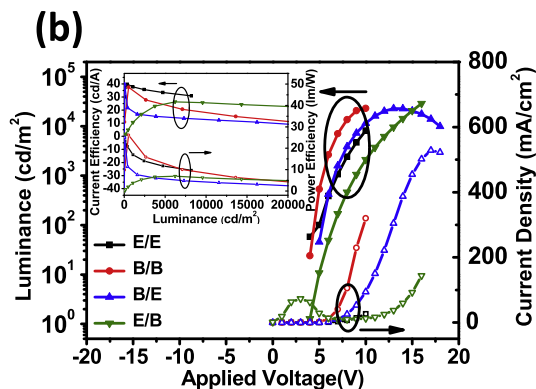
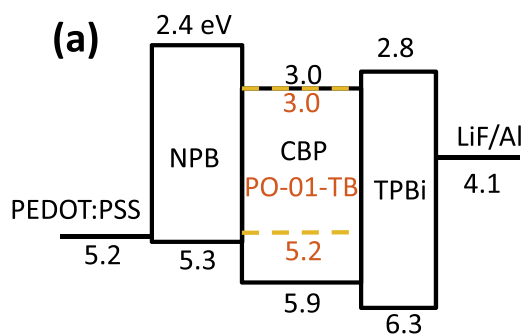


Fig. 6. (a) The device structure for orange OLED (b) The luminance and current density of orange devices with different deposition process. The inset in (b) shows the efficiency versus luminance.

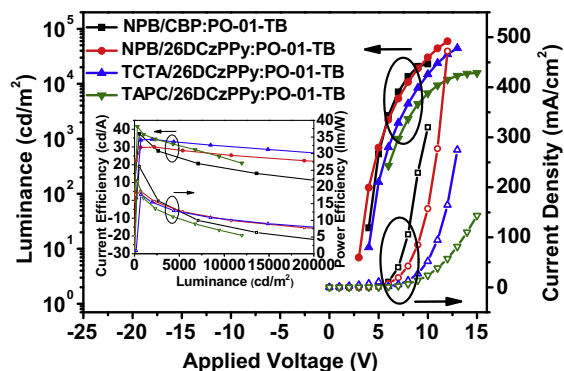


Fig. 7. The luminance and current density of orange devices with different hole transport layer and host of emission layer. The inset shows the efficiency versus luminance. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 8(c) and (d). 26DCzPPy is the host. The luminance of 1000 cd/m^2 is reached at 5 V for TAPC and 7 V for TCTA, probably due to lower hole injection barrier of TAPC. The maximal efficiency is 33 cd/A for TAPC thickness of 40 nm, with corresponding power efficiency of 20 lm/W . When the luminance is 1000 cd/m^2 the efficiencies are 31.6 cd/A and 16.5 lm/W , the efficiencies drop to 29.8 cd/A and 11.7 lm/W at 10,000 cd/m^2 . Finally we replace the green emitter $\text{Ir}(\text{mppy})_3$ by a common blue emitter FIrpic at the weight ratio of 89:11, with otherwise the same device structure. For TAPC of 30 nm, 26DCzPPy: FIrpic of

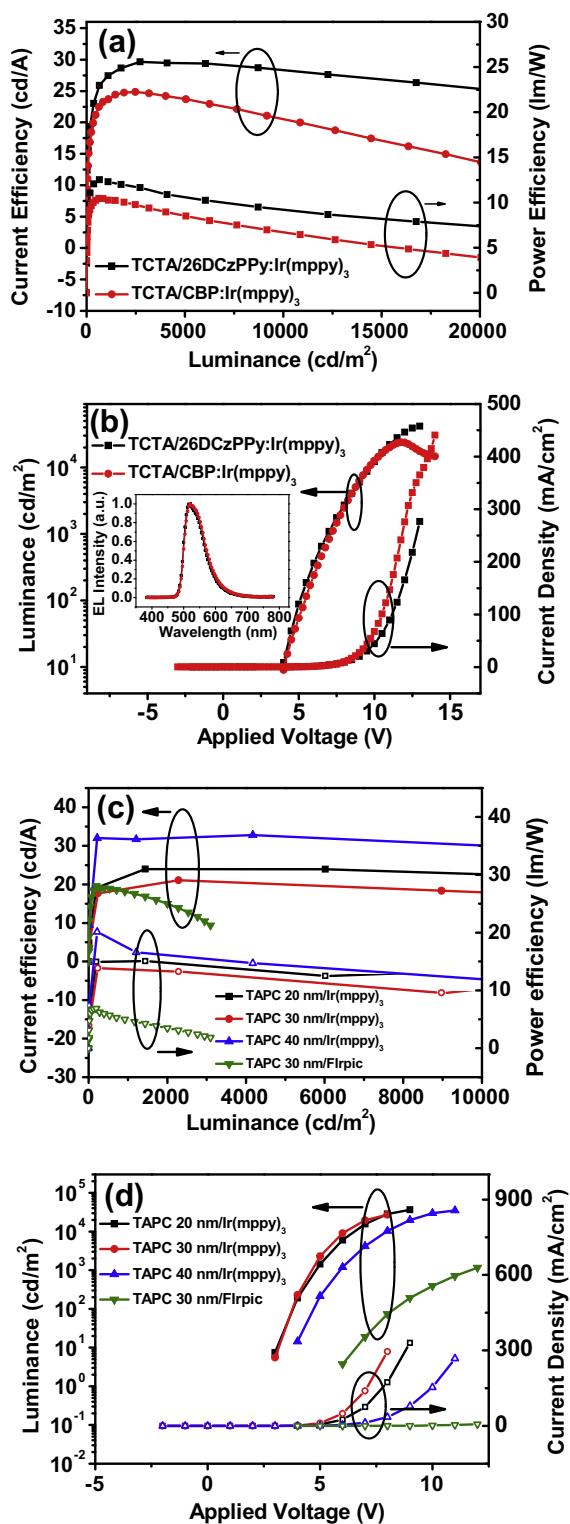


Fig. 8. The (a) efficiency versus luminance and (b) luminance and current density versus applied voltage of green devices with different host of emission layer. The inset in (b) shows the normalized EL spectra of the devices. (c) The efficiency versus luminance and (d) luminance and current density versus applied voltage for green and blue devices.

60 nm, and TPBI of 40 nm, the device performance is shown in Fig. 8(c) and (d). The maximal current efficiency is 20 cd/A at 10 V (9%) where the luminance is 392 cd/m². OLED with Flrpic emitter, TAPC hole transport layer, and 26DCzPPy by vacuum deposited was reported to achieve 20% of external quantum efficiency using a pyridine-containing electron transport layer with high mobility and deep HOMO level [12]. The common electron transport layer with high mobility and deep HOMO level [12]. The common electron transport material TPBI works well for the orange and green devices above. However it has the limit of low triplet exciton energy and insufficient hole blocking for blue devices, where the emitter Flrpic has a high triplet energy of 2.7 eV and deep LUMO level of 5.8 eV.

4. Conclusion

We show that the entire OLED multi-layer structure, originally designed and fabricated by vacuum evaporation, can be exactly copied without any chemical modification by blade coating method in solution. Only low solubility is required for the deposition and the method succeeds for most of the common unmodified small molecules. High efficiency comparable for the vacuum devices is achieved for orange, green, and blue emission. The possibility to fabricate the optimized vacuum-deposited OLED structure in solution removes the dilemma of performance and cost for OLED as a promising lighting technology.

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References

- [1] N. Rehmman, D. Hertel, K. Meerholz, H. Becker, S. Heun, Appl. Phys. Lett. 91 (2007) 103507.
- [2] K. Watanabe, D. Kumaki, T. Tsuzuki, E. Tokunaga, S. Tokito, J. Photopolym. Sci. Technol. 20 (2007) 39.
- [3] S.R. Tseng, H.F. Meng, K.C. Lee, S.F. Horng, Appl. Phys. Lett. 93 (2008) 153308.
- [4] J.D. You, S.R. Tseng, H.F. Meng, F.W. Yen, I.F. Lin, S.F. Horng, Org. Electron. 10 (2009) 1610.
- [5] J. Ouyang, T.F. Guo, Y. Yang, H. Higuchi, M. Yoshioka, T. Nagatsuka, Adv. Mater. 14 (2002) 915.
- [6] B. Park, M.Y. Han, Opt. Express 17 (2009) 13830.
- [7] S.Y. Huang, H.F. Meng, H.L. Huang, T.C. Chao, M.R. Tseng, Y.C. Chao, S.F. Horng, Synth. Met. 160 (2008) 2393–2396.
- [8] S.J. Su, H. Sasabe, T. Takeda, J. Kido, Chem. Mater. 20 (2008) 1691–1693.
- [9] D.S. Leem, S.O. Jung, S.O. Kim, J.W. Park, J.W. Kim, Y.S. Park, Y.H. Kim, S.K. Kwon, J.J. Kim, J. Mater. Chem. 19 (2009) 8824.
- [10] Z.B. Wang, M.G. Helander, J. Qiu, D.P. Puzzo, M.T. Greiner, Z.W. Liu, Z.H. Lu, Appl. Phys. Lett. 98 (2011) 073310.
- [11] E.Y. Choi, J.H. Seo, H.M. Kim, K.H. Lee, H.J. Kang, S.S. Yoon, Y.K. Kim, Jpn. J. Appl. Phys. 50 (2011) 01BC07.
- [12] S.J. Su, Y. Takahashi, T. Chiba, T. Takeda, J. Kido, Adv. Funct. Mater. 19 (2009) 1260.