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Letter

All-solution-processed blue small molecular organic light-emitting diodes with multilayer device structure

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ABSTRACT

All-solution-processed multilayer blue small molecular organic light-emitting diodes are fabricated by blade coating method. Fluorescent blue host,1-(7-(9,9′-bianthracen-10-yl)-9,9-dioctyl-9H-fluoren-2-yl)pyrene, and blue dopant, 4,4′-(1E,1′E)-2,2′-(naphthalene-2,6-diyl)bis(ethene-2,1-diyl)bis(N,N-bis(4-hexylphenyl)aniline), are used to achieve good solubility and pinhole-free thin film by solution process. The multilayer device structure with hole/electron transport layer is achieved by blade coating method without the dissolution problem between layers. The efficiency of the all-solution-processed device is 4.8 cd/A at 1200 cd/m^2, close to that by thermal deposition in high vacuum chamber. The device performance is optimized with the annealing temperature of TPBi layer at 50 °C.

Organic light-emitting diodes (OLED) and polymer light-emitting diodes (PLED) have been regarded as the candidate for the next generation light source and flat panel display. Due to the well developed materials and multilayer design of device structure, some OLED products have come into the market [1]. In general the small molecules are deposited by thermal evaporation in high vacuum chamber to form multilayer structure, including carrier transport layers, carrier blocking layers, and at least one emissive layer. The carriers can rapidly transport to emissive layer and then be confined by the blocking layers, resulting in high device efficiency. On the other hand, PLED with single layer device structure is fabricated by solution process, which can be made in large area with low cost but low device efficiency. The synthesis and purification of the polymers however are more complicated than those of small molecules. There would be great benefits to apply solution process to fabricate OLED, which combines the simple materials of OLED and cheap process of PLED [2–6]. However most of them are single layer or double layer device structure with a vacuum deposited electron transport layer. There are remaining two problems in fabricating OLED with multilayer device structure by solution process. Firstly, most small molecules could not form a thin film by solution process due to the fact that there is no chain entanglement of the small molecules. Secondly, it is difficult to form multilayer structure by solution process because of the dissolution problem between layers. The former layer would be re-dissolved by the later solution. Some modifications of the small molecules are required to form a pinhole-free layer, such as the addition of side chains or the formation of larger molecules. In this work, blue small molecular host, 1-(7-(9,9′-bianthracen-10-yl)-9,9-dioctyl-9H-fluoren-2-yl)pyrene (LT-492), and dopant, 4,4′-(1E,1′E)-2,2′-(naphthalene-2,6-diyl)bis(ethene-2,1-diyl)bis(N,N-bis(4-hexylphenyl)aniline)

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(LT-632) with side chains have been used in order to get uniform thin films. In addition to the molecular modification, many efforts have been made to fabricate multilayer structure by solution process, such as synthesis of cross-linked materials [3], water/methanol soluble materials [7], lamination method [8], liquid buffer layer [9], and blade coating method [10]. All-solution-processed OLEDs in multilayer device structure, hole transport layer (HTL)/emissive layer (EML)/electron transport layer (ETL), have been fabricated by blade coating without applying any cross-linked materials. In such devices the LiF/Al is used as the cathode, without any low work function metals like Ca, Ba, or Mg. The performance of the device by all-solution process is close to that by evaporation but the cost would be reduced dramatically due to the cheap solution process.

All-solution-processed multilayer blue light OLED with high device efficiency has been compared with its counterpart by vacuum deposition. Three devices with device structure of ITO/PEDOT:PSS/HTL/EML/ETL/LiF/Al were made to compare the different fabrication processes, including the device by all evaporation process (device A), the device with solution-processed HTL and evaporated EML/ETL (device B), and the device by all-solution process (device C). Four devices by all-solution process with different annealing temperatures of ETL layer, 20 °C (device C-1), 50 °C (device C-2), 70 °C (device C-3), and 90 °C (device C-4) for 10 min were made to optimize the device performance. Furthermore a device without ETL by solution process was made as comparison (device D). ITO is indium tin oxide and PEDOT:PSS is poly-(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (CLEVIOS™ P VP CH 8000, purchased from HC Starck). PEDOT:PSS was spin coated to form a 40 nm thin film on pre-cleaned the ITO substrate and then was baked at 100 °C for 40 min. N,N′-Bis(naphthalen-1-yl)- N,N′-bis (phenyl)- 9,9-dimethyl-fluorene (DMFL-NPB, from Luminescence Technology Corporation), acting as HTL, was dissolved in chlorobenzene to form a 20 nm film by blade and spin coating. LT-492 and LT-632 provided by Luminescence Technology Corporation, act as blue host and blue dopant individually. The 2 wt% LT-632 in the host LT-492 were dissolved in chlorobenzene and blade coated to form a 50 nm film on top of DMFL-NPB. Blade and spin coating is the process to use first blade coating to form the wet film and then spin coating until dried film is formed. Blade coating is the process only to use the blade coating without any spin coating. The DMFL-NPB and LT-492:LT-632 layers were baked at 120 °C for 10 min and 125 °C for 5 min in vacuum (10^{-3} torr). The 2,2′,2″-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi, from Luminescence Technology Corporation), acting as the ETL and hole blocking layer, was dissolved in methanol to form a 20 nm film by blade and spin coating. The film thickness by blade coating can be controlled by the solution concen-

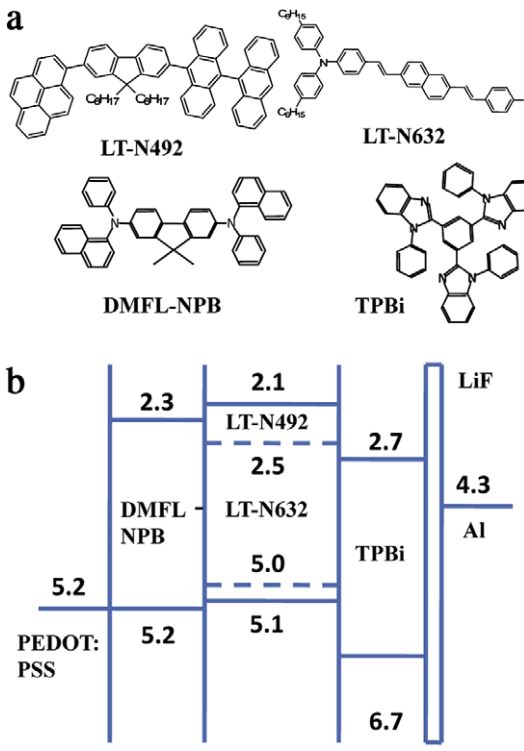

Fig. 1. (a) Chemical structures of the organic materials, and (b) schematic energy profile of the multilayer device structure design in this work. The numbers are in eV.

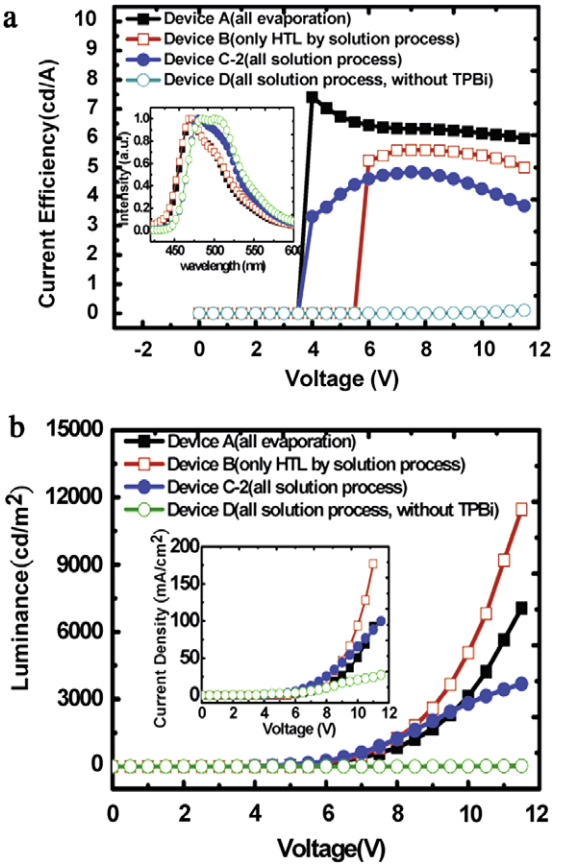

Fig. 2. Device performance of device A (solid square), device B (empty square), device C-2 (solid circle), and device D (empty circle). (a) The current efficiency. Inset is the electroluminescent spectra. (b) The luminance. Inset is the current density.

tration and the gap between substrate and blade coater. The film thickness by blade and spin coating can be controlled by the spin rate in addition to the solution concentration and the gap. The speed of blade coating is fixed at 10 cm/s. The film thicknesses are measured by a Kosaka ET4000 Surface Profiler. Fig. 1 shows the material chemical structures and schematic energy profile of the multilayer device structure. All the solution and annealing processes were performed in the glove box with low humidity (<5 ppm) and oxygen (<5 ppm). In device A all the organic layers were made by conventional thermal evaporation in the high vacuum chamber (10^{-7} torr) without any annealing process. All

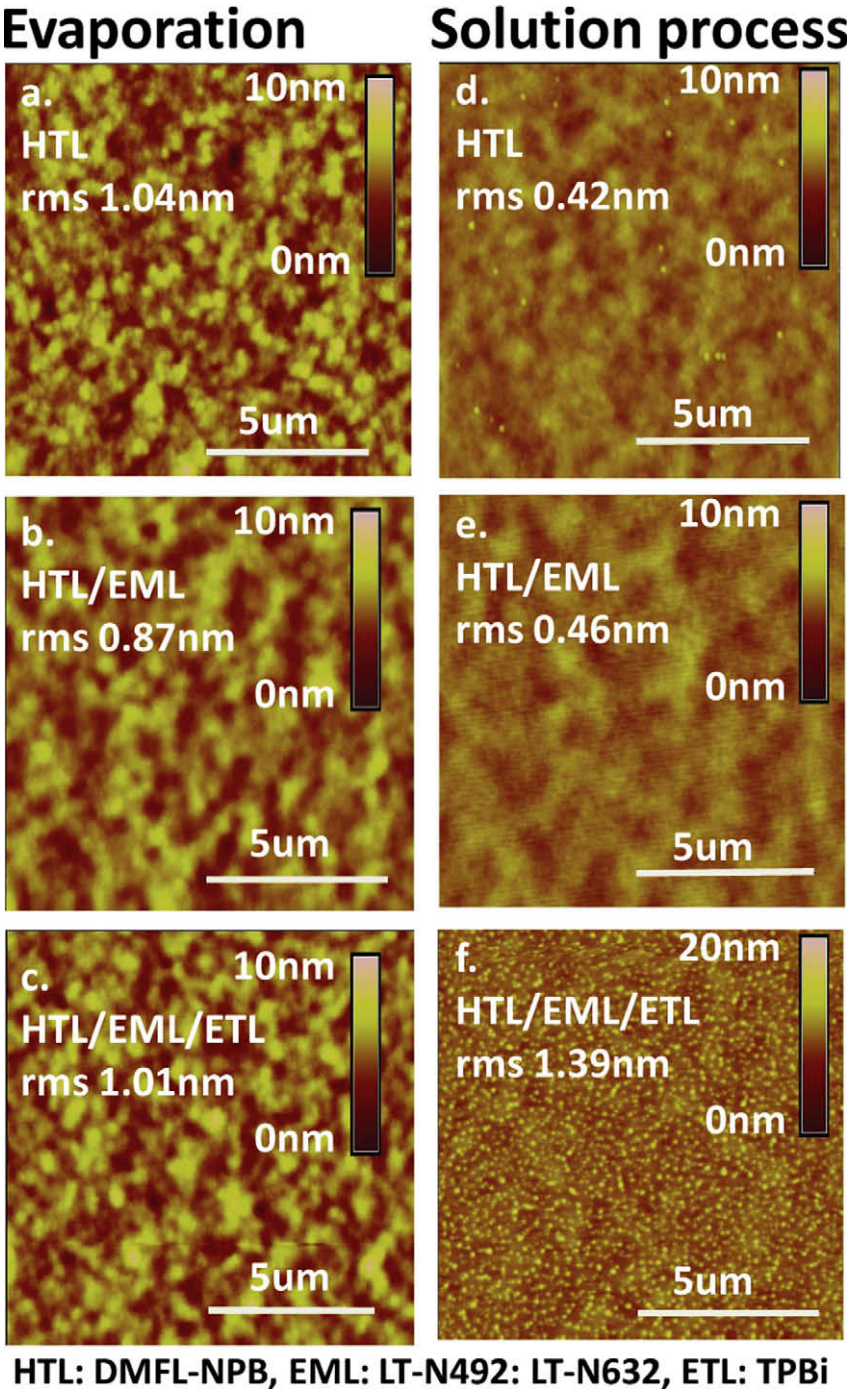

Fig. 3. AFM images of the (a) HTL, (b) HTL/EML, (c) HTL/EML/ETL by evaporation, and (d) HTL, (e) HTL/EML, (f) HTL/EML/ETL by solution process. The solution-processed ETL (TPBi) is annealed at 50 °C.

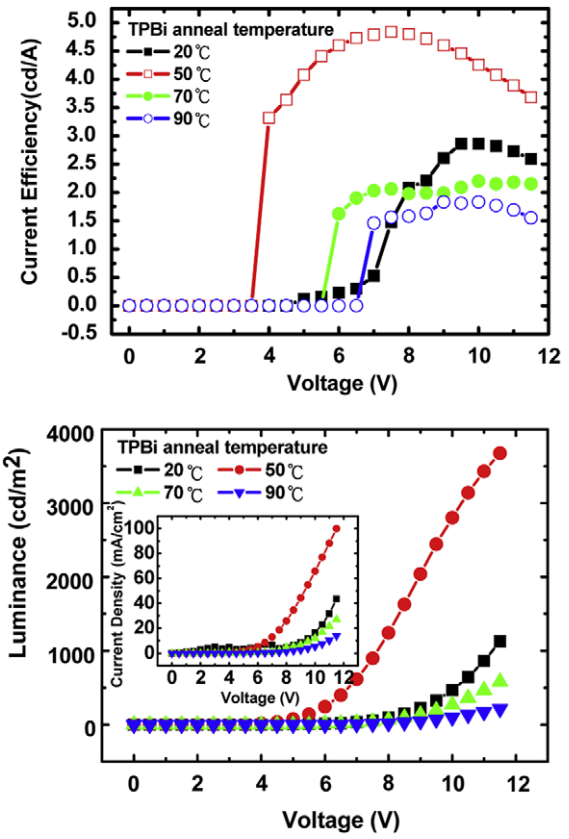

Fig. 4. Device performance of the all-solution-processed devices with different annealing temperature of TPBi, 20 °C (solid square), 50 °C (empty square), 70 °C (solid circle) and 90 °C (empty circle). (a) The current efficiency. Inset is the electroluminescent spectra. (b) The luminance. Inset is the current density.

the devices were coated with LiF(1 nm)/Al(100 nm) cathode and packaged in a glove box. Ionization potential is measured by cyclic voltammetry and electron affinity is calculated by Ionization potential plus band gap determined by the ultraviolet absorption spectrum. The electroluminescence (EL) spectra and current–luminance–voltage (*I–L–V*) characteristics are measured by a Photo Research PR650 spectrophotometer integrated with Keithley 2400 multimeter.

Fig. 2 shows the device performances of device A (all evaporation), device B (only HTL by solution process), device C-2 (all-solution process), and device D (all-solution process, without TPBi). While operating at 10 mA/cm^2, the device efficiency is 6.3 cd/A of device A, 5.6 cd/A of device B, 4.8 cd/A of device C-2, and 0.01 cd/A of device D. The maximum luminance is 7054 cd/m^2 of device A, 11,460 cd/m^2 of device B, 3677 cd/m^2 of device C-2, and 26 cd/m^2 of device D. The maximum luminance of the devices is defined as the luminance that can be achieved of the device. The luminance will decay after this maximum luminance even the bias increases. There are some damages occurred of the devices after the maximum luminance. The device performance of device D without TPBi as ETL is obviously poor, indicating TPBi layer is required to offer efficient electron injection. As can be seen in *I–V–L* relation, the current and luminance of all-solution-processed device C-2 at low bias before 9 V are about the same as those of device B and are higher than those of all-evaporated device A. At higher bias larger than 10 V, the current and luminance of device C become saturated and lower than those of device A and device B. Moreover the electroluminescent (EL) spectra of the devices with solution-processed EML (device C-2 and device D) show red-shift compared with the devices with evaporated EML (device A and device B). This may be attributed to the slight dissolution between the HTL and EML during blade coating, which might cause exciplex formation in such mixing area. The dissolution has been verified to be less than 10 nm by measuring the total film thickness. In order to study the detail of the different processes, the microscopic morphologies of each layer of device A and device C-2 have been checked by AFM. The results are shown in Fig. 3. The roughness of the evaporated layers is 1.04 nm for DMFL-NPB, 0.87 nm for LT-492 LT-632, and 1.01 nm for TPBi. The roughness of the solution-processed layers is 0.42 nm for DMFL-NPB, 0.46 nm for LT-492:LT-632, and 1.39 nm for TPBi. The morphologies of each layer by evaporation are about the same. The uniformity of the solution-processed DMFL-NPB and LT-492:LT-632 are better than the evaporated ones but a few spots still can be seen in the solution-processed DMFL-NPB. There are even more spots shown in the solution-processed TPBi layer due to the fact that there is no side chains in the TPBi molecules. We speculate that crystallization occurs in the solution-processed DMFL-NPB and TPBi and such crystallization could be regarded as one kind of impurity, which would quench the excitons. That is the reason why the efficiency decreases in device B and even more in device C-2. On the

Table 1
Performance of OLEDs in this work.

Label	HTL (DMFL-NPB)	EML (LT-492:LT-632)	ETL (TPBI)	Max. efficiency (cd/A)	Max. luminance (cd/m^2)
Device A	E[a]	E	E	7.4(4V)	7054(11.5V)
Device B	S[b]	E	E	5.6(8V)	11,460(11.5V)
Device C-1	S	S	S(20 °C)	2.9(10V)	2125(13V)
Device C-2	S	S	S(50 °C)	4.8(8V)	3677(11.5V)
Device C-3	S	S	S(70 °C)	2.3(10V)	856(13V)
Device C-4	S	S	S(90 °C)	1.8(10V)	315(13V)
Device D	S	S		0.1(11.5V)	26(11.5V)

[a] E: evaporation.
[b] S: solution process.

other hand, the crystallization in DMFL-NPB may cause higher mobility in device B and device C-2, therefore the current density is higher than that of device A at lower bias range (below 9 V). While the bias increasing, the emission zone will move to the interface between EML and TPBi due to the carrier blocking effect and the excitons would be quenched by the large crystallization of TPBi. Therefore the luminance of device C-2 becomes lower at higher bias range (after 10 V). In order to optimize the all-solution-processed OLED, devices with different annealing temperatures of TPBi layer have been made, which are device device C-1 (20 °C), C-2 (50 °C), device C-3 (70 °C), and device C-4 (90 °C). The results are shown in Fig. 4. The efficiencies while operating at 10 mA/cm^2 are 2.9 cd/A for device C-1, 4.8 cd/A for device C-2, 2.1 cd/A for device C-3, and 1.7 cd/A for device C-4. The maximum luminance are 2125 cd/m^2 for device C-1, 3677 cd/m^2 for device C-2, 856 cd/m^2 for device C-3, and 315 cd/m^2 for device C-4. The device performance of device C-1 is lower than that of device C-2, indicating that the crystallization of device C-2, as can be seen in Fig. 3f, may increase the carrier mobility and help the electron transporting. In device C-3 and device C-4 large crystallization occurs and obvious spots can be seen by naked eyes, therefore the device performances are poor due to the exciton quenching effect. the crystallization of organic film is detrimental to the device and should be avoided. The case of TPBi films annealed at 70 °C and 90 °C indeed shows the crystal formation at the scale of μm or larger in organic films which can be observed by naked eyes. The performance of the devices with TPBi at 70 °C or 90 °C shows poor efficiency. On the other hand the TPBi film at 50 °C has very small spots (much less than μm). We speculate that the films at 50 °C just start packing and cause higher carrier mobility than that annealed at 20 °C but less harmful than that with real crystals. Furthermore, according to the AFM image the morphology and roughness of HTL/EML (annealed at 125 °C, 5 min) seems to be about the same as those of HTL (annealed at 120 °C, 10 min). However the morphology and roughness changed after adding the ETL (annealed at 20 °C, 50 °C, 70 °C, or 90 °C for 10 min). Because the annealing temperature of ETL is less than that of HTL or HTL/EML, we think the roughness and morphology change should be resulted from the crystallinity change of TPBi layer, not from other layers (HTL, EML). We suggest that vapor-quality devices from solution process can be obtained with all the small molecules including hole/electron transport and emissive materials modified with side chains to get a uniform thin film without crystallization. All the device performances are summarized in Table 1.

In conclusion we have demonstrated all-solution-processed multilayer blue OLEDs by blade coating without any cross-linked materials. This kind of device combines the advantages of small molecular organic materials and large area manufacture process with low cost. Blue organic host and guest have been used with side chains to get a uniform thin film by solution process. The performance of the solution-processed device with multilayer structure can be very close to the evaporated one, and the cost of the solution-processed can be reduced dramatically.

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