

S. WANG
Y.Q. LIU✉
X.B. HUANG
S.L. XU
J.R. GONG
X.H. CHEN
L. YI
Y. XU
G. YU
L.J. WAN
C.L. BAI
D.B. ZHU

Organic light-emitting diodes with improved hole-electron balance by using molecular layers of phthalocyanine to modify the anode surface

Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P.R. China

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ABSTRACT By using the Langmuir–Blodgett (LB) technique, well-defined molecular layers of 2,9,16-tri(tert-butyl)-23-(10-hydroxydecyloxy)phthalocyanine were fabricated. These LB films have been employed to modify an anode surface of organic light-emitting devices. The insertion of LB films between an indium tin oxide (ITO) and hole-transport layers leads to an increase in device efficiency as a result of an improvement of the balanced carrier injection. An external quantum efficiency of 0.88% and a brightness of 10 840 cd/m² for a device with a structure of ITO/two LB layers/*N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD)/tris(8-hydroquinolinato)aluminium (Alq₃)/Al were obtained, while the external quantum efficiency and brightness for the device without LB layers of ITO/TPD/Alq₃/Al were 0.51% and 5744 cd/m², respectively.

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1 Introduction

Since multilayer organic light-emitting devices (OLEDs) were developed [1], active research had been performed to improve the device performance [2–6]. For fabricating efficient devices, it is necessary to enhance charge injection efficiency at both OLED cathode/organic and anode/organic interfaces. A number of techniques have been developed. These included adding injection/transporting layers and using metals with low work functions as the cathode [7–11]. The insertion of phthalocyanines (Pcs) film fabricated by evaporation or sputter-grown has demonstrated excellent improvement of hole injection [12, 13]. Our previous study demonstrated that the addition of a self-assembled Pc monolayer was also a good method to enhance this carrier injection [14]. In film formation, the Langmuir–Blodgett

(LB) technique is attractive because it offers the fabrication of an organized assembly with a controlled thickness at molecular dimensions and with well-defined molecular orientation and the preparation of hetero-structures by successive deposition of monolayers [15–17]. In this paper, we report the use of LB technique to introduce single and several molecular layers between indium tin oxide (ITO) anode and the hole-transport layer (HTL) of a two-layer OLEDs, and investigate their effects on the device performance. Results show that LB techniques can yield well-defined molecular layers, and that the introduction of these layers between the anode and HTL can significantly improve the charge injection balance and enhance the maximum external quantum efficiency. Moreover, different numbers of layers also leads to different effects on the operating voltage and external quantum efficiency of devices.

2 Results and discussion

Figure 1 shows the molecular structure of 2,9,16-tri(tert-butyl)-23-(10-hydroxydecyloxy) phthalocyanine (HO-Pc) [14]. In order to get organized assembly at the air-water interface, the hydrophobic phthalocyanine was substituted by hydrophilic hydroxydecyloxy unit. The surface pressure-area (π -*A*) isotherms for this molecule at 23 °C are shown in Fig. 2. The steeply inclining part corresponds to the formation of the solid film and the high surface pressure of the collapse point of the floating layer up to 44 mN/m, indicates the good film-forming behavior of the Pc and the formation of a stable monolayer on the water surface. From the π -*A* isotherm, the limiting area per repeat unit is determined to be 0.71 nm². This value is useful for estimating the configuration of Pc molecules at the air-water interface. It had been reported that the diagonal distance across a molecule of tert-butyl-substituted phthalocyanine was approximately 1.95 nm, as calculated by Hua et al. [18]. Although this phthalocyanine molecule is substituted

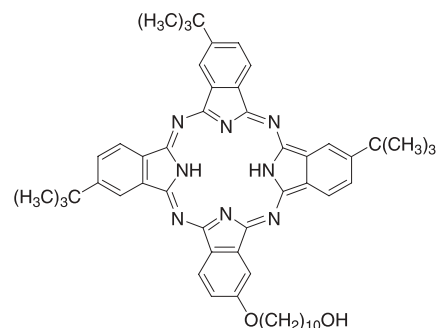
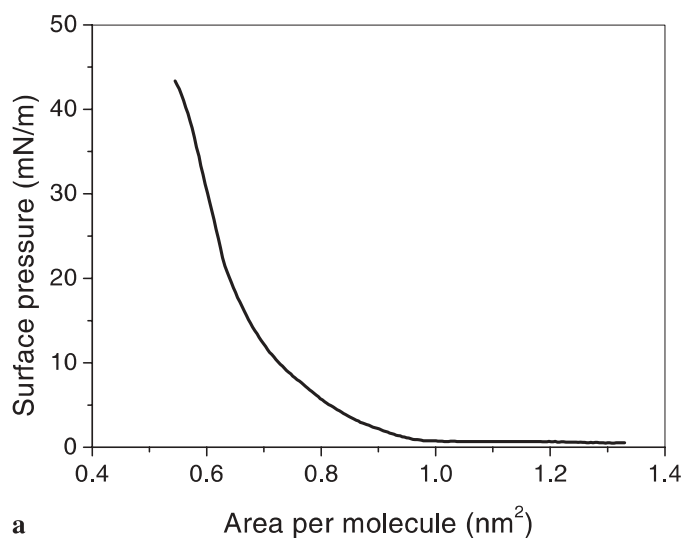
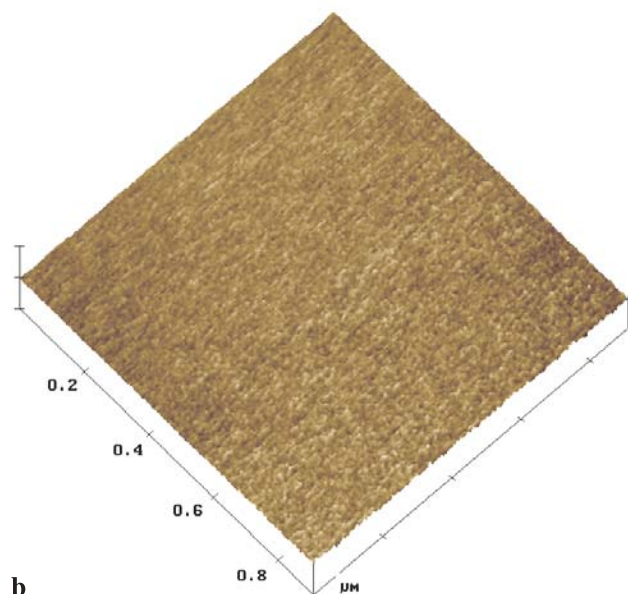


FIGURE 1 Chemical structure of HO-Pc

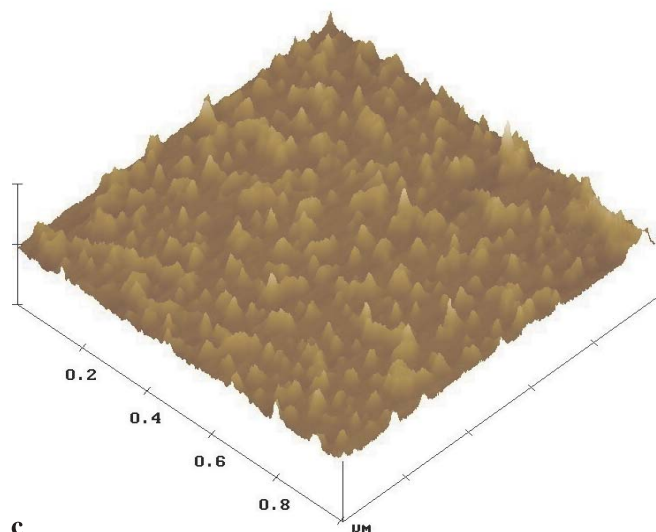
✉ Fax: +86-10/6255-9373, E-mail: liuyq@iccas.ac.cn



a



b



c

FIGURE 2 a Surface pressure-area isotherm of HO-Pc at 23 °C. b and c AFM images of pure mica and the Pc monolayer

by one hydroxydecyloxy group with three tert-butyl groups, its structure can be nearly regarded as square. If this molecule is fully extended and lies flatly on the water surface, its limiting area is about 1.904 nm^2 . The limiting area per repeat unit obtained from the π -A curve is smaller than that of the estimated one. We assumed that the molecules formed an edge-on structure at the air-water interface, and tilted by 68° against the surface normal. The monolayer conformation of Pcs on the water surface has the hydrophilic hydroxydecyloxy moieties in the molecule placed on the water surface with the hydrophobic phthalocyanine units standing up from the water surface to the air phase. The π - π interaction made the conjugated planes facing each other to form the π -stacked aggregates. Its thickness is about 1.54 nm.

In order to better understand the film property of Pc layers, the monolayer Pc film was fabricated on the mica surface, and its assembly investigated by using an atomic force microscopy (AFM). Figure 2b and c show the AFM images of pure mica and the Pc monolayer. The surface roughness of pure mica and this film on mica substrate is about 0.092 and 0.228 nm by tipping mode AFM. From Fig. 2, it can be seen that well-defined monolayer was achieved.

Schematic fabrication of OLEDs is shown in Fig. 3, where *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) and tris(8-hydroquinolinato)aluminium (Alq_3) were used as the electron-transporting and emitting layer, and TPD as the hole-transporting layer. Two kinds of devices with the structure of ITO/(LB layer)_n/TPD/ Alq_3 /Al and ITO/TPD/ Alq_3 /Al were performed. The light emission was observed when devices were operated under a forward bias (positive voltage applied to ITO electrode), demonstrating a typical diode behavior. Their electroluminescence (EL) spectra are similar and the maximums are located at 510 nm, which indicates that the emission originates from the emission of Alq_3 . Figure 4 shows the current and brightness as a function of operating voltage for a set of devices with bare ITO, or ITO coated with monolayer, double-layer, and three-layer LB layers. The thickness of the Pc layer was about within a range of 1.5–4.5 nm. There are significant dif-

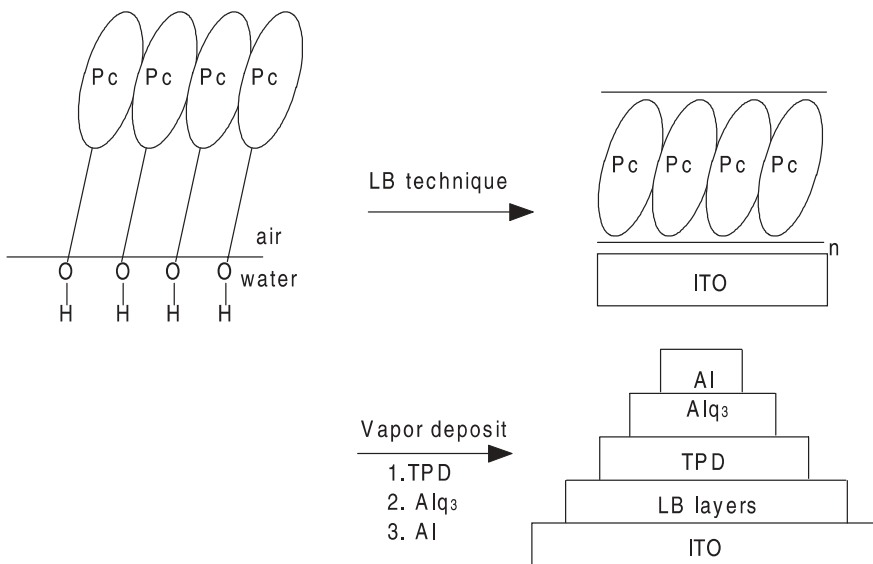
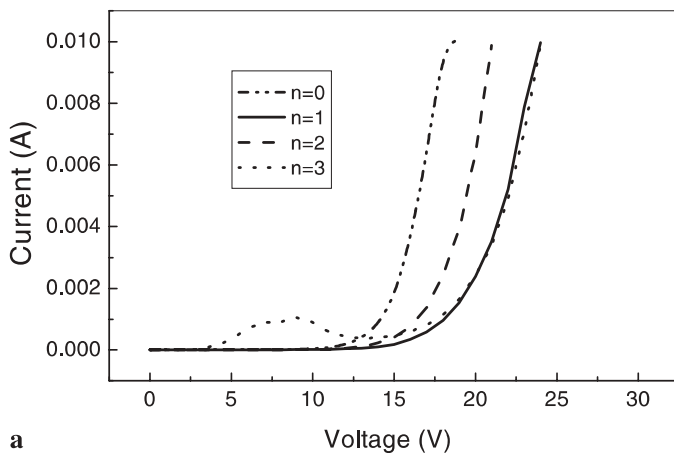
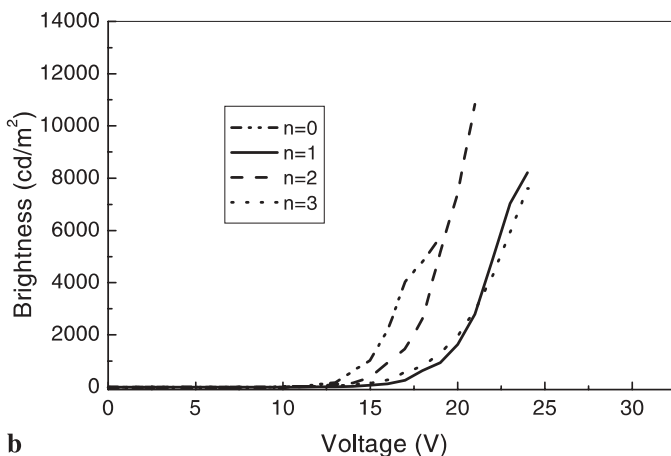


FIGURE 3 Procedure for the fabrication of OLEDs with Pc LB layers



a



b

FIGURE 4 a Current and b forward light output vs. voltage plots for ITO/TPD/Alq₃/Al, and ITO/(LB layer)_n/TPD/Alq₃/Al

ferences in current-voltage (I - V) and brightness-voltage (L - V) characteristics in devices with different Pc layers. It can be seen that by inserting layers of Pcs between ITO and TPD both the

I - V and B - V curves are shifted towards higher voltage, which demonstrates that Pcs layers are less hole injection structures than conventional ITO. The maximum light output for Pc-based devices

was also increased. Interestingly, it can be seen that the effect of a single layer substantially increased the operating voltage. As the number of Pc layers is increased from one to two, the operating voltage falls rapidly. Finally, at three Pc layers, the operating voltage increases again. Devices coated with two Pc layers showed the highest brightness of 10 840 cd/m² at 21 V, while that of an ITO-based device is 5744 cd/m² at a voltage of 19 V. Compared to the devices without Pc layers, the stability of the EL device is largely improved too.

Figure 5 shows the external quantum efficiency of these devices. From Fig. 5, it is easily noted that the increase of external efficiencies for the devices of ITO/(LB layer)_n/TPD/Alq₃/Al is quite similar to that for the device of ITO/TPD/Alq₃/Al. At the initial stage, the efficiency increases very quickly and then slows down with an increase in current density. The effect of Pc layers substantially increased the maximum quantum efficiency. It had been reported that for the bare ITO electrode, it is likely that hole injection is far more efficient than electron injection from the cathode [19–21]. Figure 4a demonstrated that these LB layers were less hole injection structures than conventional ITO. So these Pc layers enhance quantum efficiency via better balanced hole- and electron-injection rather than by facilitating hole injection or interfacial stability. Interestingly, as the number of Pc layers is then increased from one to two, the maximum quantum efficiency reaches the maximum. Further increase leads to the decrease of device quantum efficiency.

As the widely used anode material in OLEDs, ITO also has some disadvantages as revealed in previous literature [22]. Quantum efficiency of bare electrode devices is degraded by leakage currents and ITO-HTL interfacial chemical reaction. The ITO functionalization addresses all of these deficiencies, with the principal effect being to correct the hole/electron injection imbalance [19]. In these devices with Pc LB layers, the effect of surface states, the increase of device thickness, and the insulation of the Pc long hydroxydecyloxy chain was also included. The insertion of Pc layers limited excess hole injection and enhanced the quantum efficiency with higher driving voltages.

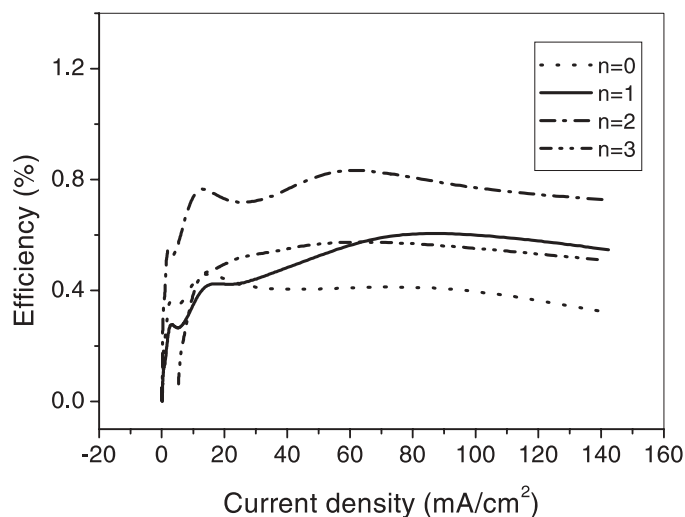


FIGURE 5 External quantum efficiency vs. current density plots for ITO/TPD/Alq₃/Al and ITO/(LB layer)_n/TPD/Alq₃/Al

The change of operating voltage and efficiency with the increase of Pc layers was related to complex effects combined with modification of the ITO surface states. The reason for the decreased quantum efficiency of devices with three layers was related to the negative effect of surface states, as the number of the surface states was increased.

3 Experimental

The synthesis of 2,9,16-tri(tert-butyl)-23-(10-hydroxydecyloxy) phthalocyanine was carried out according to the reported method [14]. Surface pressure-area isotherm measurements and deposition experiments were performed on a fully automatic KSV-5000 instrument (Finland). HO-Pc dissolved in chloroform (0.6 mM) was spread onto double-distilled water. At a constant pressure of 22 mN/m, the floating layer on the subphase was transferred to the ITO substrate by the vertical dipping method at a speed of 1 mm/min. The ITO glasses were cleaned by ultrasonically in water, alcohol, chloroform, and acetone, successively for 10 min and dried. LEDs were fabricated using Alq₃ as the electron-transporting and emitting layer, TPD as the hole-

transporting layer, Al as the cathode and the ITO, or ITO coated with different Pc layers, as the anode. TPD, Alq₃, and Al electrodes were deposited by vacuum evaporation at a pressure below 10⁻⁵ Torr. The active area of the devices was about 7 mm². EL spectra were recorded on an Hitachi F-4500 fluorescence spectrophotometer with the LED forward biased. The power of EL emission was measured using a Newport 2835-C multifunction optical meter. Current-voltage characteristics were measured with a Hewlett Packard 4140B semiconductor parameter analyzer. All the measurements were performed under ambient atmosphere at room temperature.

4 Conclusion

In conclusion, this study demonstrates that one can use the LB technique to introduce well-defined molecular Pc layers to modify the interface between anode and organic layers for hole injection. Two molecular layers is considered to be optimal for interface engineering; as it offers the most balanced carrier injection with the highest brightness.

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REFERENCES

- 1 C.W. Tang, S.A. Slyke: *Appl. Phys. Lett.* **51**, 913 (1987)
- 2 C.L. Lee, K.B. Lee, J.J. Kim: *Appl. Phys. Lett.* **77**, 2280 (2000)
- 3 L.S. Hung, M.G. Mason: *Appl. Phys. Lett.* **78**, 3732 (2001)
- 4 G.E. Jabbour, Y. Kawabe, S.E. Shaheen, J.F. Wang, M.M. Morrell, B. Kippelen, N. Peyghambarian: *Appl. Phys. Lett.* **71**, 1762 (1997)
- 5 V. Bliznyuk, B. Ruhstaller, P.J. Brock, U. Scherf, S.A. Carter: *Adv. Mater.* **11**, 1257 (1999)
- 6 P.K.H. Ho, M. Granstrom, R.H. Friend, N.C. Greenham: *Adv. Mater.* **10**, 769 (1998)
- 7 J.E. Malinsky, G.E. Jabbour, S.E. Shaheen, J.D. Anderson, A.G. Richter, N.R. Armstrong, B. Kippelen, P. Dutta, N. Peyghambarian, T.J. Marks: *Adv. Mater.* **11**, 227 (1999)
- 8 W.-L. Yu, J. Pei, Y. Cao, W. Huang: *J. Appl. Phys.* **89**, 2343 (2001)
- 9 S.C. Kim, G.B. Lee, M.-W. Choi, Y. Roh, C.N. Whang, K. Jeong, J.-G. Lee, S. Kim: *Appl. Phys. Lett.* **78**, 1445 (2001)
- 10 W. Brütting, H. Riel, T. Beierlein, W. Riess: *J. Appl. Phys.* **89**, 1704 (2001)
- 11 A. Ulman: *Chem. Rev.* **96**, 1533 (1996)
- 12 L.H. Zhu, H.Q. Tang, Y. Harima, K. Yamashita, D. Hirayama, Y. Aso, T. Otsobu: *Chem. Commun.* 1830 (2001)
- 13 L.L. Duan, S.J. Garrett: *Langmuir* **17**, 2986 (2001)
- 14 X.B. Huang, Y.Q. Liu, S. Wang, S.Q. Zhou, D.B. Zhu: *Chem. Eur. J.* **8**, 4179 (2002)
- 15 A. Aoki, Y. Tamagawa, T. Miyashita: *Macromolecules* **35**, 3686 (2002)
- 16 A.J. Pal, T. Östergård, J. Paloheimo: *Appl. Phys. Lett.* **69**, 1137 (1996)
- 17 J.M. Ouyang, L. Li, Z. Tai, Z. Lu, G.M. Wang: *Chem. Commun.* 815 (1997)
- 18 Y.L. Hua, G.G. Roberts, M.M. Ahmad, M.C. Petty: *Philos. Mag. B* **53**, 105 (1986)
- 19 J.E. Malinsky, G.E. Jabbour, S.E. Shaheen, J.D. Anderson, A.G. Richter, T.J. Marks, N.R. Armstrong, B. Kippelen, P. Dutta, N. Peyghambarian: *Adv. Mater.* **11**, 227 (1999)
- 20 L.J. Rothberg, A.J. Lovinger: *J. Mater. Res.* **11**, 3174 (1996)
- 21 J.R. Sheats, H. Antoniadis, M. Hueschen, W. Leonard, J. Miller, R. Moon, D. Roitman, A. Stocking: *Science* **273**, 884 (1996)
- 22 X. Zhou, J. He, L.S. Liao, M. Lu, Z.H. Xiong, X.M. Ding, X.Y. Hou, F.G. Tao, C.E. Zhou, S.T. Lee: *Appl. Phys. Lett.* **74**, 609 (1999)