

Journal of Materials Chemistry C

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Electrochemically Deposited Film as Interface Layer to Improve the Performance of Polymer Light-emitting Diodes

Tiancheng Yu, Xiaoyan Wu, Ying Lv, Linlin Liu*, Luyang Du, Jiadong Zhou, Zengqi Xie, Yuguang Ma*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

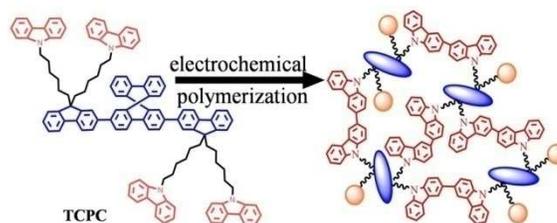
DOI: 10.1039/b000000x

Insoluble electrochemically cross-linked thin film is successfully applied as interface layer between PEDOT:PSS and light emitting layer in solution-processed polymer light-emitting diodes for enhanced device performance.

1 Introduction

To improve the device performance of polymer light-emitting diodes (PLEDs), sandwich-like multilayer device structure is usually applied by integrating different functional layers,¹ including the active light-emitting layer and charge carrier injecting/blocking and transporting layers. Polyethylene dioxythiophene-polystyrene sulfonate (PEDOT:PSS), which is a water-soluble conducting material and was successfully introduced in PLEDs by Cao et al.,² is now commonly used as the hole injection layer (HIL) in solution processible PLEDs, due to its reasonable work function (5.2 eV), good transparency in visible region, variable conductivity, good hole injection ability, flattening effects, and excellent air-stability.³ Even though PEDOT:PSS really reduces the hole injection barrier between indium tin oxide (ITO) anode and emitting layer (EML), many problems still exist. Firstly, it is acidic⁴ and may quench the excitons.⁵ Secondly, the redundant electrons can pass through the EML to attack the PEDOT:PSS, resulting in byproduct, which may cause the degradation of the active materials, and thus is bad for the devices stability.⁶ However, it is quite difficult to find a better material as HIL to completely replace the PEDOT:PSS for the moment. So it is suggested that a thin interface layer can be used to isolate the EML from PEDOT:PSS to increase the device performance.⁷ The prerequisite for the interface layer should be insoluble in the spin-coating of the subsequent light-emitting layer in PLEDs. To meet above requirement, a series of thin film was utilized, involving in situ chemical cross-linking layers,^{8,9} solvent-selective insoluble layers,^{10,11,12} and the thermal bake-out layers.¹³

In this work, we uniquely deposited a thin layer by in situ electrochemical polymerization (ECP) method from 2,7-bis(9,9-bis(6-(9H-carbazol-9-yl)hexyl)-9H-fluorene-2-yl)-9,9'-spirobifluorene TCPC (Scheme 1), a kind of material synthesized in our



Scheme 1 Schematic of electrochemical polymerization of multiple carbazole functionalized monomer to form a cross-linked structure.

group,¹⁴ on PEDOT:PSS as an interface layer to increase the performance of solution processible PLEDs. Compared to the above mentioned processes preparing a thin interface layer, such as in situ chemical cross-linking, our ECP method has a few advantages. Firstly, the thickness of the thin film can be easily modulated through controlling the amount of charge passed through the cell.^{15,16} Secondly, the ECP thin film is completely cross-linked through electrochemical coupling reaction between electro-active groups (i.e. carbazole in this work),¹⁷ thus it is insoluble in common solvents used to dissolve the light-emitting polymer, and is convenient for the spin-coating of subsequent functional layer. Thirdly, the surface of the ECP film is rather smooth with surface roughness similar to that of spin-coated film,¹⁸ which is favorable to the performance of devices.

2 Experimental section

TCPC and P-PPV were synthesized in our laboratory as previous reported.^{14, 18} Caesium fluoride (CsF) was purchased commercially and was used without purifying. The PLED devices were fabricated using the procedures as follows: indium tin oxide (ITO) coated glass substrates were cleaned prior to device fabrication by sonication in acetone, detergent, distilled water, and isopropyl alcohol in sequence, and finally dried in an oven. After treated with an oxygen plasma for 4 min, a 40 nm thick polyethylene dioxythiophene-polystyrene sulfonate (PEDOT:PSS) (Bayer Baytron 4083) layer was spin-coated on the ITO-coated glass substrates at 2500 rpm for 30 s, the substrates were subsequently dried at 120°C for 20 min in air and then transferred to a N₂-glovebox. Then the electrochemical polymerization was performed using a standard one-compartment, three-electrode electrochemical cell attached to a CHI 760D Electrochemical Workstation. An Ag/Ag⁺ non-aqueous electrode was used as a reference electrode, ITO/PEDOT:PSS (40 nm) was used as the

Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, P. R. China.
Tel: +86-20-22237036; Fax: +86-20-87110606
E-mail: ygma@scut.edu.cn; msluill@scut.edu.cn

working electrode, and titanium metal was used as the counter electrode (area: $\sim 3 \text{ cm}^2$). A mixture of TCPC and TBAPF₆ (0.1 M) with CH₂Cl₂ and acetonitrile was used as the electrolyte solution. The electrochemical polymerization was processed by CV mode and after the electrochemical polymerization process, the resulting ECP layer was washed with a mixture of CH₂Cl₂ and acetonitrile (3:2, V:V), to remove any unreacted precursors and supporting electrolytes, and then dried with nitrogen. The whole ECP process was conducted in the glove box. After the ECP thin layers with different thickness were deposited on PEDOT:PSS, the P-PPV was spin-coated from *p*-xylene solution on the ECP thin layer at 1000 r/min for 30 s with the thickness of about 80 nm. And then the CsF and Al layer were deposited by the vacuum evaporation method. The background pressure of the chamber was under 10^{-4} Pa during the deposition process.

The layer thickness of the deposited material was monitored in situ using an oscillating quartz thickness monitor. The current density–brightness–voltage (J–B–V) characteristics were measured by a Keithley 236 source measurement unit. The electroluminescent (EL) spectra were measured using a PR-705 Spectroscan spectrometer. The device fabrication, except PEDOT:PSS coating, was carried out in a nitrogen atmosphere dry-box (Vacuum Atmosphere Co.) containing less than 10 ppm oxygen and moisture. The atomic force microscopy (AFM) image was recorded on a Seiko SPA 400 with an SPI 3800 probe station in tapping mode (dynamic force mode).

3 Results and discussion

TCPC is a kind of wide band-gap electro-polymerizable precursor (3.0 eV), which is suited as interface materials in multiple PLEDs. Firstly, we investigated the electrochemical behavior of TCPC using PEDOT:PSS coated ITO as the working electrode. As shown in Figure S1, the onset oxidation potential is at 0.79 V (vs Ag/Ag⁺), and there are three oxidation peaks located in 0.92 V, 1.07 V, 1.25 V, assigned to the oxidation of carbazole and trifluorene backbone, respectively. A reduction peak appears at 0.49 V assigned to the reduction of dimeric carbazole cation. These results indicate that the redox behavior of TCPC on the

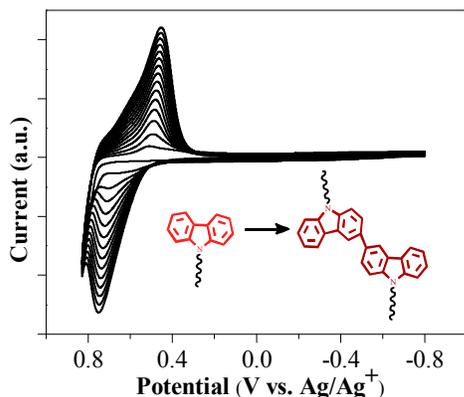


Fig. 1 Cyclic voltammogram for electrochemical polymerization under conditions such as: 1 mg mL⁻¹ TCPC, 0.1 M TBAPF₆, scanning potential region -0.8 V to $+0.83 \text{ V}$, mixed solvents $V_{\text{CH}_2\text{Cl}_2}:V_{\text{CH}_3\text{CN}} = 2:3$, scanning rate 200 mV/s. The inset shows the electrochemical couple of carbazole.

working electrode of ITO/PEDOT:PSS was almost the same as

that on bare ITO as shown in our reports.¹⁷ Thus the ECP process was conducted within the potential range of -0.8 V to $+0.83 \text{ V}$. The high potential was set as $+0.83 \text{ V}$ that is high enough for oxidation of the carbazole groups to form the carbazolyl radical cations, but still lower than the oxidation potential of trifluorene backbone in order to keep the electronic structure of TCPC. The dimeric carbazole cation is formed through the coupling reaction of carbazolyl radical cation, and is reduced to dimeric carbazole, indicated by the reduction peak at $+0.49 \text{ V}$ during the inverse scan from positive to negative potential. As shown in Figure 1, the appearance of a new oxidation peak at $+0.69 \text{ V}$ during the second cyclic voltammogram scanning confirms the forming of dimeric carbazole on ITO/PEDOT:PSS substrate. The increasing of peak current in subsequent scanning shows that more and more dimeric carbazole units are formed on PEDOT:PSS substrate. Owing to four reactive carbazole groups in a TCPC molecule, a cross-linked layer was deposited successfully on PEDOT:PSS layer, as illustrated in Scheme 1. The ECP layer is insoluble in common organic solvents due to the highly cross-linked structure, which is demonstrated by the identical absorption spectra (Figure S3) of ECP layer before and after rinse with *p*-xylene (that is used to dissolve P-PPV for fabrication of the EML layer through spin-coating method). So it is a stable interface to avoid the redissolution in solution-processible multiple layer PLEDs.

The atomic force microscopy height images of PEDOT:PSS and the ECP thin film on PEDOT:PSS with different thickness are shown in Figure 2 and Figure S2. The root-mean-square roughness (R_{rms}) values were 1.2 nm for PEDOT:PSS and 1.7 nm for ECP thin film of about 12 nm, indicating that the ECP thin film is a smooth interlayer, comparative to the spin-coated film which is favorable to fabricate stable multilayer PLEDs.

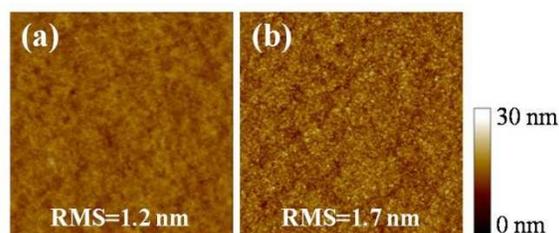


Fig. 2 AFM height images of (a) ITO/PEDOT:PSS and (b) ITO/PEDOT:PSS/ECP thin films. The thickness of the ECP thin layer for (b) is about 12 nm. The size of the images is $5 \times 5 \mu\text{m}$. The ECP film is prepared under conditions such as: 1 mg mL⁻¹ TCPC, 0.1 M TBAPF₆, scanning potential region -0.8 V to $+0.83 \text{ V}$, mixed solvents $V_{\text{CH}_2\text{Cl}_2}:V_{\text{CH}_3\text{CN}} = 2:3$, scanning rate 200 mV/s.

The PLEDs were then fabricated based on the device configuration of ITO/PEDOT:PSS (40 nm)/ECP thin film (x nm)/P-PPV (80 nm)/CsF (1.5 nm)/Al (120 nm), where poly[2-(4-(3',7'-dimethyloctyloxy)-phenyl)-*p*-phenylenevinylene] (P-PPV) acted as a classical light-emitting layer.¹⁸ ECP thin film was used as the interface layer and its thickness is tuned by controlling the scanning cycles, namely X for different devices. Here $X=0$ nm means that there was no ECP layer between PEDOT:PSS and P-PPV, which was actually a control device to compare with others. The reason why the P-PPV was selected as the light-emitting material is that a specific chemical interaction may occur between PPV and PEDOT:PSS, creating defect states in interface region which would partly quench PPV photoluminescence.¹⁹

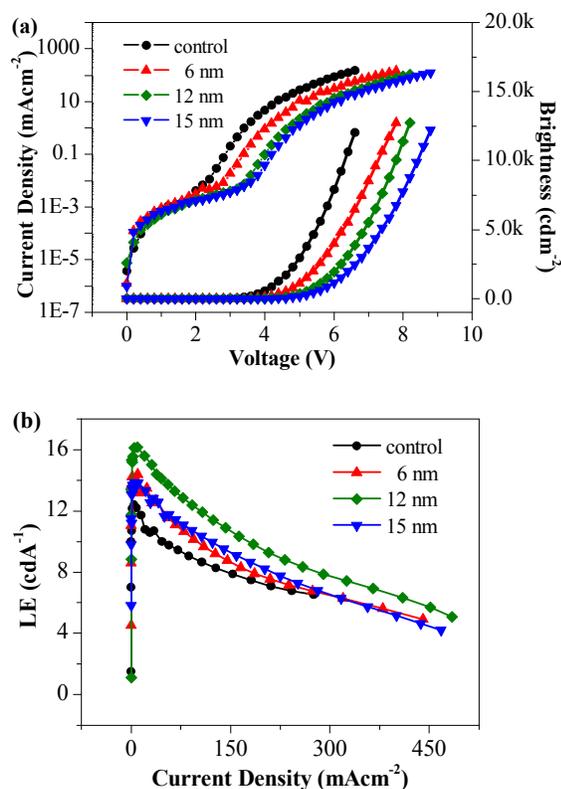


Fig. 3 (a) Current density–brightness–voltage (J–B–V) and (b) Luminous efficiency–current density (LE–J) characteristic of ITO/PEDOT:PSS (40 nm)/ECP thin film (x nm)/P-PPV (80 nm)/CsF (1.5 nm)/Al (120 nm), x = 0, 6, 12, 15 nm.

The thickness of ECP thin layer for fabricating PLEDs and the detailed performance data for different devices, including turn-on voltage, maximum brightness, maximum luminous efficiency, are included in Table 1. The J-B-V and LE-J characteristic are depicted in Figure 3. As a result, the ECP thin layer as interface layer enhances the performance of device effectively. The optimal performance comes from the device with ECP thin layer of about 12 nm as interface layer. The maximum luminous efficiency of device incorporating ECP layer is improved from 12.3 cd/A (X=0 nm) to 16.2 cd/A (X=12 nm), about an increase of 32%. Furthermore, the maximum brightness keeps nearly the same as the control device (~12000 cd/m²), although the turn-on voltage becomes slight higher from 2.8 V to 3.9 V, which may be ascribed to the increased film thickness. As for the enhancement of performance, it is speculated that there are two factors about it. On one hand, the ECP thin layer indeed plays a role in isolating the PEDOT:PSS from the emissive P-PPV, as we had expected. The fluorescence quantum yield of ITO/PEDOT:PSS (40 nm)/P-PPV (80 nm) is 16.6%, while that of ITO/PEDOT:PSS (40 nm)/ECP Layer (~12 nm)/P-PPV (80 nm) is 17.9%, showing an increasing of 7.9% and demonstrating the isolation effect of ECP thin layer. On the other hand, in view of the fact that conductivity of ECP thin layer is lower according to the electrochemical impedance spectroscopy (EIS) measurement,²⁰ it is speculated that the ECP thin film also acts as a hole blocking layer. As we know, P-PPV is a typical p-type semiconductor in which the holes are the majority carrier. So the insertion of low conductive

ECP thin layer can cause the most easily injected holes to partly accumulate at the PEDOT:PSS/ECP layer interface until efficient injection of electrons becomes favorable, reducing leakage currents and promoting the balance of positive and negative carrier injected into the device, which is crucial to the performance of device.²¹ We also prepared the hole only device of ITO/PEDOT:PSS (40 nm)/ECP thin film (x nm)/P-PPV (80 nm)/MoO₃ (10 nm)/Al (100 nm), the decreasing of current density in J-V characteristic of Figure 3a and current in I-V curve of hole only device, as shown in Figure S4, demonstrates the above-mentioned speculation on hole blocking effect of ECP thin layer. In addition, the insertion of ECP thin layer has not changed the peaks position of electroluminescence of devices, as is shown in Figure S5.

Table 1. The performance of PLEDs device of ITO/PEDOT:PSS (40 nm)/ECP thin film (x nm)/P-PPV (80 nm)/CsF (1.5 nm)/Al (120 nm), x = 0, 6, 12, 15 nm.

ECP layer thickness [nm]	Turn-on Voltage [V]	Bmax cd/cm ² [at voltage]	LEmax cd/A [at voltage]
Control	2.8	12056 (6.6 V)	12.3 (3.8 V)
6	3.3	12725 (7.8 V)	14.3 (4.6 V)
12	3.9	12734 (8.2 V)	16.2 (5.6 V)
15	4.1	12199 (8.8 V)	13.8 (5.8 V)

4 Conclusion

In summary, we developed a new way to deposit an insoluble, neat thin film on PEDOT:PSS through the electrochemical coupling reaction of the electro-active groups. The ECP thin film successfully isolates the PEDOT:PSS from the light-emitting layer, avoiding the negative effect of PEDOT:PSS on the performance of PLEDs. Meanwhile, the ECP thin layer also acted as a hole blocking layer, balancing the carriers injected into the device. The combination of isolation effect and blocking effect improved the performance of solution-processible PLEDs, which promises electrochemically deposited isolation layer for using in the development of high performance organic optoelectronic devices.

Acknowledgements

We thank the supports from the Natural Science Foundation of China (21334002, 51303057), National Basic Research Program of China (973 Program) (2013CB834705), Fundamental Research Funds for the Central Universities (2013ZM0009), Guangdong Natural Science Foundation (S2012030006232), and Introduced Innovative R&D Team of Guangdong (201101C0105067115).

Notes and references

- C. W. Tang and S. A. Vanslyke, *Appl. Phys. Lett.*, 1987, **51**, 913.
- Y. Cao, G. Yu, C. Zhang, R. Menon and A. J. Heeger, *Synth. Met.*, 1997, **87**, 171.
- B. H. Zhang, W. M. Li, J. W. Yang, Y. Y. Fu, Z. Y. Xie, S. B. Zhang and L. X. Wang, *J. Phys. Chem. C.*, 2009, **113**, 7898.
- a) S. Wu, S. H. Han, Y. N. Zheng, H. Zheng, N. L. Liu, L. Wang, Y. Cao and J. Wang, *Org. Electron.*, 2011, **12**, 504; b) P. Tehrani, A. Kancierzewska, X. Crispin, N. D. Robinson, M. Fahlman and M.

- Berggren, *Solid State Ionics.*, 2007, **177**, 3521
- 5 J. S. Kim, R. H. Friend, I. Grizzi and J. H. Burroughes, *Appl. Phys. Lett.*, 2005, **87**, 023506.
- 6 J. H. Burroughes, Presented at the Asia Display/IMID'2004, August 23
- 5 27, 2004, session 11. 4.
- 7 S. Nau, N. Schulte, S. Winkler, J. Frisch, A. Vollmer, N. Koch, S. Sax and E. J. W. List, *Adv. Mater.*, 2013, **25**, 4420.
- 8 A. W. Hains, H. Y. Chen, T. H. Reilly III and B. A. Gregg, *ACS Appl. Mater. Interfaces.*, 2011, **3**, 4381.
- 10 9 K. Zhang, C. M. Zhong, S. J. Liu, A. H. Liang, S. Dong and F. Huang, *J. Mater. Chem. C.*, 2014, DOI: 10.1039/c3tc32022g.
- 10 Z. C. He, C. M. Zhong, S. J. Su, M. Xu, H. B. Wu and Y. Cao, *Nat. Photonics.*, 2012, **6**, 591.
- 11 N. Cho, H. L. Yip, J. A. Davies, P.D. Kazarinoff, D.F. Zeigler, M. M.
- 15 Durban, Y. Segawa, K. M. O'Malley, C. K. Luscombe and A. K. Y. Jen, *Adv. Energy Mater.*, 2011, **1**, 1148.
- 12 B. J. Woerfolk, T. C. Hauger, K. D. Harris, D. A. Rider, J. A. M. Fordyce, S. Beaupré, M. Leclerc and J. M. Buriak, *Adv. Energy Mater.*, 2012, **2**, 361.
- 20 13 a) A. Köhnen, M. Irion, M. C. Gather, N. Rehmman, P. Zacharias and K. Meerholz, *J. Mater. Chem.* 2010, **20**, 3301; b) Y.-H. Niu, M. S. Liu, J. W. Ka, J. Bardeker, M. T. Zin, R. Schofield, Y. Chi and A. K.-Y. Jen, *Adv. Mater.*, 2007, **19**, 300; c) Y. H. Niu, M. S. Liu, J. W. Ka, A. K.-Y. Jen, *Appl. Phys. Lett.*, 2006, **88**, 093505.
- 25 14 S. Tang, M. R. Liu, P. Lu, H. Xia, M. Li, Z. Q. Xie, F. Z. Shen, C. Gu, H. P. Wang, B. Yang and Y.G. Ma, *Adv. Funct. Mater.*, 2007, **17**, 2869.
- 15 C. C. You, P. Espindola, C. Hippus, J. Heinze and F. Würthner, *Adv. Funct. Mater.*, 2007, **17**, 3764.
- 16 M. Li, S. Tang, F. Shen, M. Liu, W. Xie, H. Xia, L. Liu, L. Tian, Z.
- 30 Xie, P. Lu, M. Hanif, D. Lu, G. Cheng and Y. Ma, *Chem. Commun.*, 2006, 3393.
- 17 M. Li, S. Tang, F. Shen, M. Liu, W. J. Xie, H. Xia, L. Liu, L. Tian, Z. Xie, P. Lu, M. Hanif, D. Lu, G. Cheng and Y. Ma, *J. Phys. Chem. B.*, 2006, **110**, 17784.
- 35 18 H. B. Wu, F. Huang, Y.Q. Mo, W. Yang, D.L. Wang, J. B. Peng and Y. Cao, *Adv. Materials.*, 2004, **16**, 1826.
- 19 A. van Dijken, A. Perro, E. A. Meulenkaamp and K. Brunner, *Org. Electron.*, 2003, **4**, 131.
- 20 T. Feng, B. Xiao, Y. Lv, Z. Xie, H. Wu and Y. Ma, *Chem. Commun.*,
- 40 2013, **69**, 6283.
- 21 Q. Wu, *Crit. Rev. Solid State Mater. Sci.*, 2013, **38**, 318.

45