

Supporting information:

Highly luminescent network films from electrochemical deposition of peripheral carbazole functionalized fluorene oligomer and their applications for light-emitting diodes

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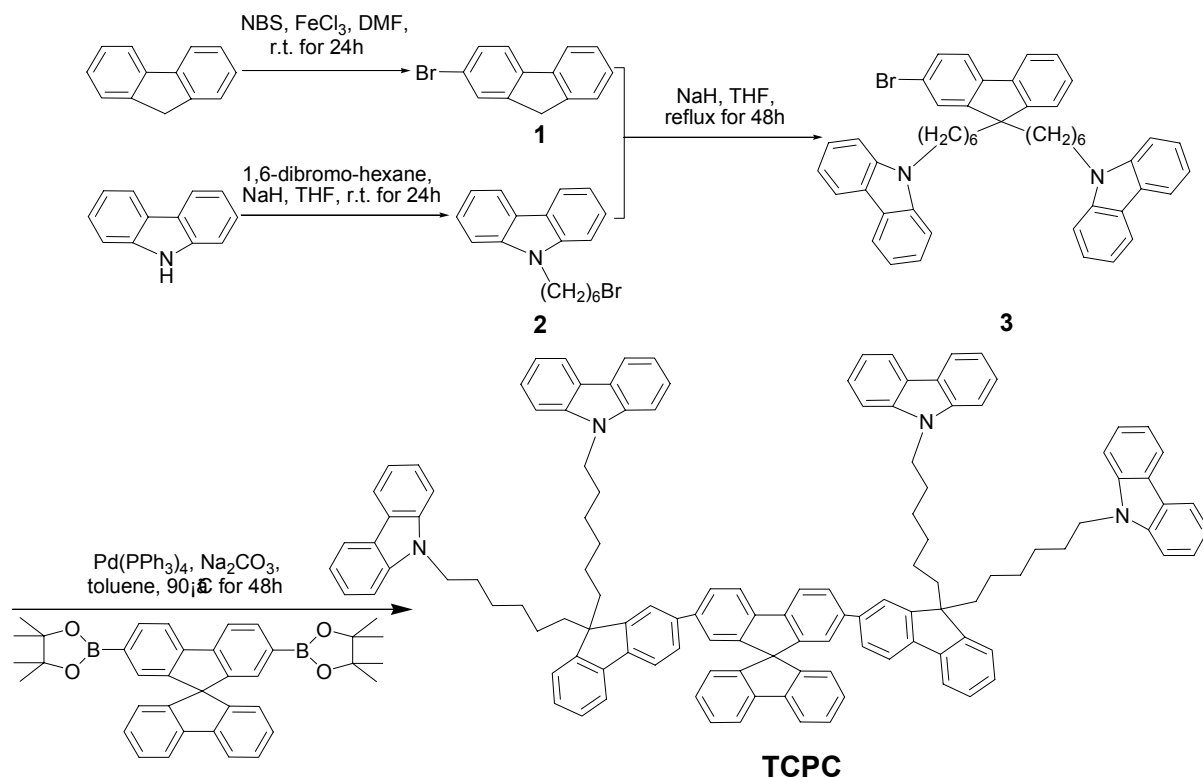
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1. Instruments for Characterization of ED precursor and ED films.

The ^1H NMR spectra were recorded on AVANCZ 500 spectrometers at 298 K by utilizing deuterated chloroform (CDCl_3) or Dimethyl Sulphoxide (DMSO-d_6) as solvent and tetramethylsilane (TMS) as standard. The compounds were characterized by Flash EA 1112, CHNS-O elemental analysis instrument. FTIR spectra were recorded on Perkin-Elmer spectrophotometer in the $400\text{-}4000\text{ cm}^{-1}$ region using a powdered sample in KBr plate. The LC/TOF/MS mass spectra were recorded using an APPLIED BIOSYSTEMS QSTAR instrument. UV-vis absorption spectra were recorded on UV-3100 spectrophotometer. Fluorescence measurements were carried out with RF-5301PC. Atomic force microscopic (AFM) images were taken in air and ambient conditions by tapping mode using a Nanoscope II, Digital Instrument system equipped with a $5\times 5\text{ }\mu\text{m}^2$ scanner and a silicon nitride tip. The field emission scanning electron microscope (FESEM) images were taken by JSM-6700F.

2. Synthesis of ED precursor TCPC

The synthesis starting from commercially available fluorene and carbazole is shown in **Scheme S1**. 2-bromofluorene (**1**), N-(6-bromohexane)-carbazole (**2**) and 9,9'-bis(N-carbazolyl-decyl)-2-bromofluorene (**3**) were obtained with high yields. Finally, Suzuki coupling reaction between monomer (**3**) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-spirobifluorene (preparation and purification according to previous reports)^{S1} was performed in a biphasic system (toluene/aqueous Na₂CO₃) with Pd(PPh₃)₄ as a catalyst precursor, gives the compound **TCPC** as solid white powder after chromatographic purification. All compounds were verified by ¹H NMR spectroscopy and mass spectrometry as well as elemental analysis.



Scheme S1. The route of synthesis of compound **TCPC**

2-bromofluorene (1): ¹H NMR (500 MHz, CDCl₃, ppm): δ7.766-7.751 (d, 1H, Ar-H), δ7.682 (s, 1H, Ar-H), δ7.650-7.634 (d, 1H, Ar-H), δ7.546-7.531 (d, 1H, Ar-H), δ7.510-7.491 (d, 2H,

Ar-H), δ 7.398-7.368 (t, 1H, Ar-H), δ 7.342-7.310 (t, 1H, Ar-H), δ 3.890 (s, 2H, Ar-CH₂-Ar).

MS (m/z) 244.2. Anal. Calcd. for C₁₃H₉Br: C, 63.70; H, 3.70 Found: C, 63.59; H, 3.76.

N-(6-bromohexane)-carbazole (2): ¹H NMR (500 MHz, CDCl₃, ppm): δ 8.11-8.09 (d, 2H, Ar-H), δ 7.47-7.45 (t, 2H, Ar-H), δ 7.40-7.39 (d, 2H, Ar-H), δ 7.23-7.21 (t, 2H, Ar-H), δ 4.31-4.30 (t, 2H, N-CH₂), δ 3.36-3.35 (t, 2H, Br-H), δ 1.92-1.86 (m, 2H, CH₂), δ 1.84-1.78 (m, 2H, CH₂), δ 1.49-1.44 (m, 2H, CH₂), δ 1.42-1.38 (m, 2H, CH₂). Anal. Calcd. for C₁₈H₂₀NBr: C, 65.46; H, 6.10; N, 4.24 Found: C, 65.44; H, 6.10; N, 4.12.

9,9'-bis(N-carbazolyl-hexyl)-2-bromofluorene (3): ¹H NMR (500 MHz, DMSO-d₆, ppm): δ 8.12-8.10 (d, 4H, Ar-H-car), δ 7.76-7.75 (d, 1H, Ar-H-flu), δ 7.72-7.71 (d, 1H, Ar-H-flu), δ 7.57 (s, 1H, Ar-H-flu), δ 7.48-7.47 (d, 4H, Ar-H-car), δ 7.42-7.39 (t, 4H, Ar-H-car), δ 7.28-7.25 (m, 4H, Ar-H-flu), δ 7.18-7.15 (t, 4H, Ar-H-car), δ 4.26-4.23 (m, 4H, N-CH₂), δ 1.83-1.82 (m, 4H, CH₂), δ 1.53-1.52 (m, 4H, CH₂), δ 1.01 (m, 8H, CH₂), δ 0.40-0.38 (m, 4H, CH₂). Anal. Calcd. for C₄₉H₄₇N₂Br: C, 79.12; H, 6.37; N, 3.77 Found: C, 79.13; H, 6.32; N, 3.18.

TCPC: ¹H NMR (500 MHz, DMSO-d₆, ppm): δ 8.16-8.15 (d, 2H, Ar-H-flu), δ 8.09-8.07 (d, 8H, Ar-H-car), δ 7.92-7.91 (d, 2H, Ar-H-flu), δ 7.80-7.78 (d, 2H, Ar-H-flu), δ 7.68-7.65 (t, 4H, Ar-H-flu), δ 7.48 (s, 2H, Ar-H-flu), δ 7.42-7.39 (d, 8H, Ar-H-car), δ 7.36-7.33 (t, 8H, Ar-H-car), δ 7.30-7.27 (m, 4H, Ar-H-flu), δ 7.24-7.17 (m, 6H, Ar-H-flu), δ 7.14-7.11 (t, 8H, Ar-H-car), δ 7.05-7.01 (t, 2H, Ar-H-flu), δ 6.86 (s, 2H, Ar-H-flu), δ 6.69-6.67 (d, 2H, Ar-H-flu), δ 4.18-4.15 (m, 8H, N-CH₂), δ 1.79-1.78 (m, 8H, CH₂), δ 1.46-1.45 (m, 8H, CH₂), δ 0.94 (m, 16H, CH₂), δ 0.45-0.43 (m, 8H, CH₂). FT-IR (λ , cm⁻¹): 3048, 2929, 2852, 1595, 1483, 1463, 1451, 1347, 1323, 1228, 1152, 1119, 819, 747, 723. MALDI-TOF-MS (M+H)⁺ = 1641.8 (100%). Anal. Calcd. for C₁₂₃H₁₀₈N₄: C, 89.96; H, 6.63; N, 3.41 Found: C, 89.73; H, 6.92; N, 3.36.

3. Electrochemical properties and ED experiment

3.1 General experiments

Supporting electrolytes TBAPF₆ and TBABF₄ were purchased from Aldrich and dried for 24 h under vacuum before use. The electropolymerizable precursor compound, **TCPC**, has a chemical structure as shown in Scheme 1. The MeCN proved to be the most successful solvent for the polymerization process among the solvents studied. Solvent can play an important role in stabilizing radical cations^{S2} and in this case the carbazole radical cations are stable in MeCN to react further to form polymer. In order to improve the solubility of **TCPC** we have used a mixed solvent of MeCN and CH₂Cl₂ (*v/v* = 3/2), which were carefully purified and purged by dry nitrogen prior to the electrochemical measurements.

The cyclic voltammetry (CV) experiments were performed using a standard one-compartment, three-electrode electrochemical cell given by a BAS 100B/W Bioanalytical Systems. In all cases, potential refer to the system Ag/0.1 M AgNO₃ in acetonitrile calibrated versus the ferrocene redox couple. The ITO (~1 cm²) was used as working electrode; the counter electrode was a titanium metal (area: ~3 cm²). In the electrochemical experiment 1 mg/mL **TCPC**/0.1 M TBABF₄ or TBAPF₆ solution in a mixture of acetonitrile and CH₂Cl₂ (*v/v* = 3/2) was used. After **ED** process, the resulting **ED** film was then washed with acetonitrile to remove any unreacted precursors.

3.2 Electrochemical behavior of TCPC (first scan)

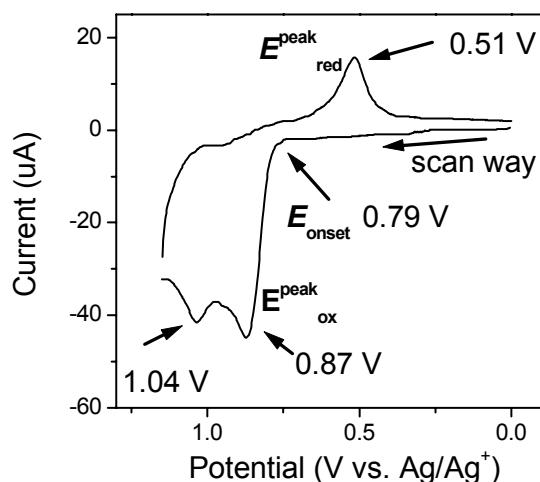


Figure S1. CV of the TCPC using ITO as the working electrode. TBABF₄ was used as the supporting electrolyte. Scan rate: 50 mV/s. When the potential sweep was scanned between 0 and 1.15 V, the oxidation onset potential at 0.79 V and the oxidation peak at 0.87 V were attributed to the cation of carbazole,^{S3} the oxidation peak at 1.04 V was attributed to the oxidation of trifluorene, the reduction peak at 0.51 V was attributed mainly to the reduction of the dicationic state.^{S3}

3.3 ED of TCPC

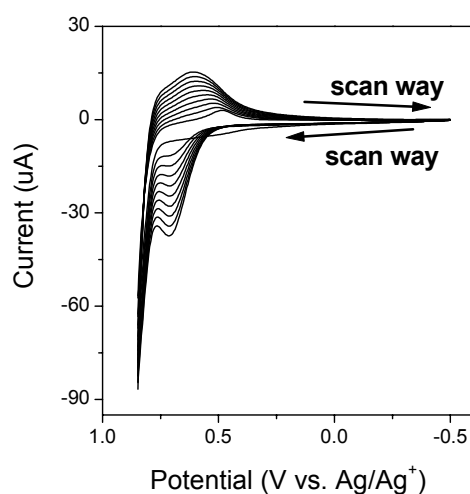


Figure S2. CV of the TCPC using ITO as the working electrode. TBABF₄ was used as the

supporting electrolyte. Scan rate: 50 mV/s. From the second sweep, a new oxidation peak merged at 0.71 V at a less anodic potential than the starting oxidation of TCPC. Recurrent sweeps led to a progressive increased of this new redox system because the TCPC was ED on ITO substrate.

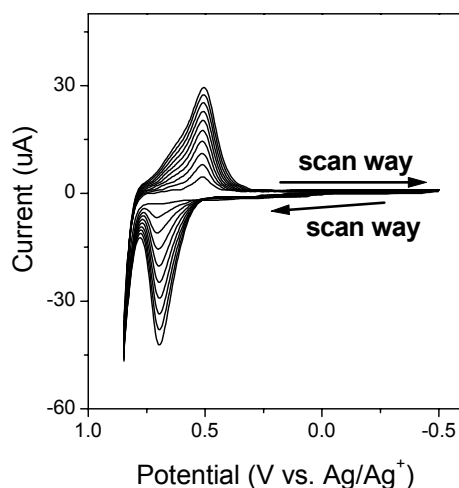


Figure S3. CV of the TCPC using ITO as the working electrode. TBAPF₆ was used as the supporting electrolyte. Scan rate: 50 mV/s. As the number of scanning cycles increasing, the reduction peak current clearly increased and the reduction potential was unchanged when the TBABF₆ was used as the supporting electrolyte. This indicated that dedoping was better when TBAPF₆ was used as the supporting electrolyte during ED.

4. FT-IR spectra of ED films

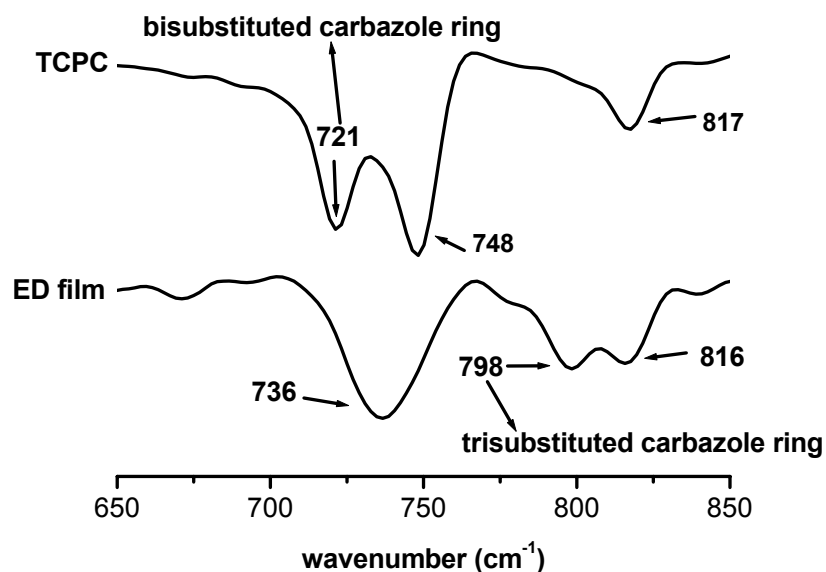


Figure S4. FT-IR absorption spectrum of TCPC and its ED film prepared by potentiostatic potential (0.85 V). The TBABF₄ was used as supporting electrolyte in ED process. The peaks at 721 cm⁻¹ and 798 cm⁻¹ were attributed to the bisubstituted and trisubstituted carbazole ring, respectively. The peak at 721 cm⁻¹ did not appear after ED. This observation indicated that polymerization proceed from the 3 and 6 positions.

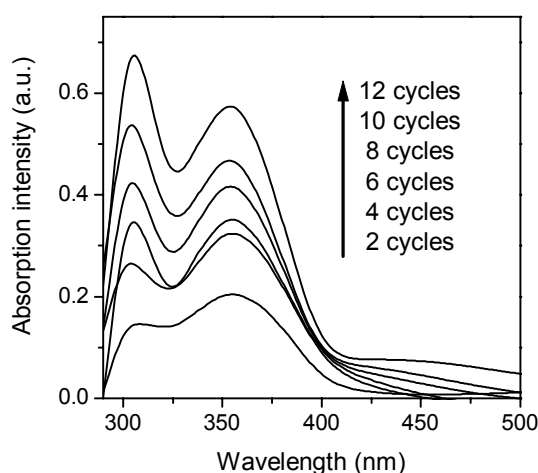


Figure S5. The absorption spectra of ED films on ITO using different scan cycles. TBABF₄ was used as supporting electrolyte. Scan rate: 50 mV/s. Scan range: -0.5 V~ 0.85 V. The absorption spectra of ED films with increased scan cycles. It can be seen that the absorption

intensities attributed to trifluorene backbone is increased as scan cycles increases, demonstrating that the thickness of **ED** film can be controlled by scan cycles.

5.. Optimization of the morphology

5.1 Supporting electrolyte

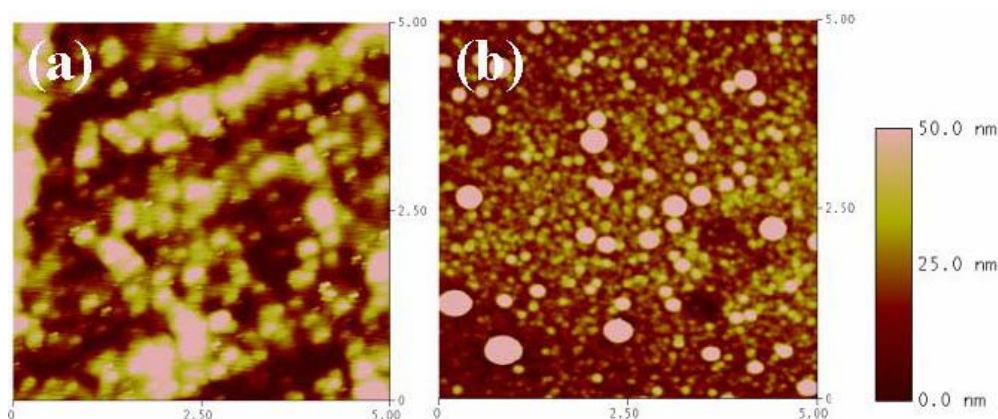


Figure S6. The AFM images of **ED** films on ITO by CV using TBABF₄ (A) and TBAPF₆ (B) as supporting electrolytes. Scan rate: 50 mV/s (cycles 10). Scan range from -0.5 V to 0.85 V. From **Figure S6** can be seen that the film obtained by TBAPF₆ as supporting electrolyte has more smooth morphology with roughness of 11.2 nm (RMS) as compared with 22.4 nm (RMS) for film obtained using TBABF₄ as supporting electrolyte. Combined the electrochemical and optical investigations, TBAPF₆ is more suitable supporting electrolyte for preparing high quality **ED** films. Thus the **ED** films prepared by using TBAPF₆ as supporting electrolyte are used for further morphologic investigations.

5.2 Scan cycles

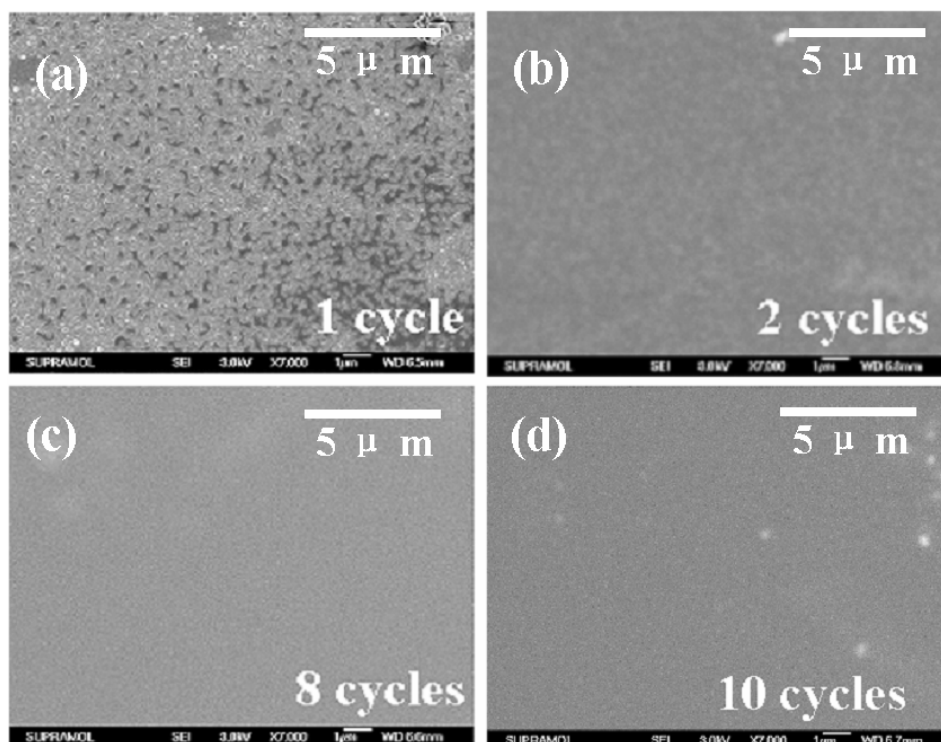


Figure S7 The SEM micrographs of **ED** films using ITO as working electrolyte were obtained from different scan cycles. The TBAPF₆ is used as supporting electrolyte. The **ED** film obtained after first cycle show a loose morphology (**Figure S7a**), which cannot fully cover the electrode. With increasing in scan cycles, the film became more and more smooth as shown in **Figure S7c** and **Figure S7d** for **ED** films obtained by 8 and 10 cycles respectively. This indicated that electrochemically deposited films show an ability of “self-reparation”: the electropolymerization products filled up preferentially the lacunas because of relative high potentials in these positions.

5. 3 Scan rate

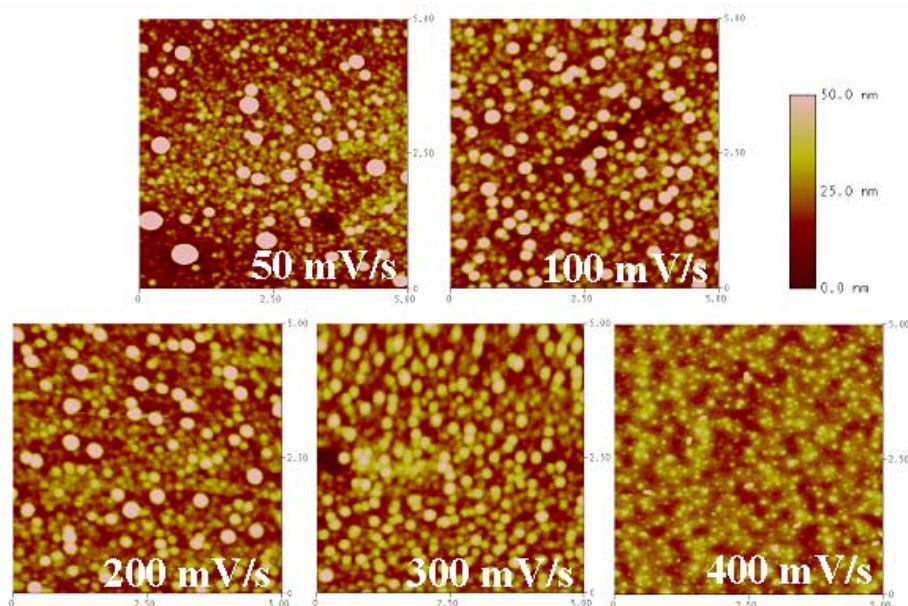


Figure S8. The AFM images of **ED** films on ITO by CV using TBAPF_6 as supporting electrolytes. Scan rate: 50 mV/s (cycles 10); 100 mV/s (cycles 20), 200 mV/s (cycles 40), 300 mV/s (cycles 60) and 400 mV/s (cycles 80). Scan range from -0.5 V to 0.85 V. A further investigation for these **ED** films, the magnified view by AFM (**Figure S7d**) shows that **ED** film (relative SEM image as shown in **Figure S7d**) has the roughness of 11.2 nm RMS and the large ellipsoidal grains on **ED** film are observed. We find that increasing scan rates result in the decrease of the sizes of these ellipsoidal grains, and the decrease of the roughness of films. The **ED** film obtained by scan rate of 400 mV/s gives very smooth surface with roughness of just 2.8 nm RMS, which is similar to film obtained by spin-coating from solution. It should be noted that the films used for AFM investigation were prepared by different scan cycles, e.g. 10 cycles as scan rate of 50 mV/s, 20 cycles as scan rate of 100 mV/s, and 80 cycles as scan rate of 400 mV/s, in order to get the **ED** films with close thickness.

8. Electroluminescence devices

These LEDs had structures of ITO/**ED** films/Ba(5 nm)/Al(200 nm). Such **ED** films for LEDs were prepared by CV model (TCPC: 1 mg/mL, TBAPF_6 as supporting electrolytes, **ED** area:

$\sim 100 \text{ mm}^2$, 52 cycles by CV, scan rate: 200 mV/s, scan range: from -0.2 V to 0.85 V). 52 scan cycles (about 12 min) give an **ED** film with thickness of $\sim 100 \text{ nm}$.

The electroluminescence (EL) spectra and luminance were recorded by a PR-650 spectrometer. The emission area of the device is 0.04 cm^2 , defined by the overlapping area of the anode and cathode. The normalized EL spectrum is shown in **Figure S9**. The device exhibited pure blue emission at λ_{max} 427 nm with CIE coordinates of (0.16, 0.08). The external quantum efficiency for this device is 0.72%. The device showed typical diode-like current density and voltage (J-V) characteristics having a turn-on voltage of 8 V. Under positive voltage over 8 V, blue emission can be observed and emission intensity was increased with climbing driving voltage. The achieved maximum luminescence and luminous efficiency was $4224 \text{ cd/m}^2 @ 17 \text{ V}$ and $0.47 \text{ cd/A} @ 11.5 \text{ V}$, respectively. (see **Figure S10**)

When TBABF₄ was used as supporting electrolyte, the device exhibited blue emission at $\lambda_{\text{max}} = 436 \text{ nm}$ (see **Figure S9**), and the achieved maximum luminescence and luminous efficiency is $134 \text{ cd/m}^2 @ 16.5 \text{ V}$ and $0.016 \text{ cd/A} @ 11 \text{ V}$ after optimizing electrochemical parameter (see **Figure S11**), respectively.

In order to compare the **ED** films properties with spin-coating method, we have fabricated some LEDs, which had structures of ITO/PEDOT:PSS(30 nm)/TCPC($\sim 80 \text{ nm}$)/Ba(5 nm)/Al(200 nm), where the conducting polymer polyethylene dioxythiophene/polystyrene sulfonate (PEDOT : PSS) is used as the hole-injection layer. The normalized EL spectrum is shown in **Figure S12**. The device exhibits pure blue emission at $\lambda_{\text{max}} = 416 \text{ nm}$ with CIE coordinates of (0.16, 0.05). The turn-on voltage is 4.5 V. The achieved maximum luminescence and luminous efficiency is $78 \text{ cd/m}^2 @ 7 \text{ V}$ and $0.11 \text{ cd/A} @ 4.5 \text{ V}$, respectively

for this device. (see **Figure S13**) The external quantum efficiency for this device is 0.31%. Thus it can be seen that the maximum luminescence and luminous efficiency are improved obviously.

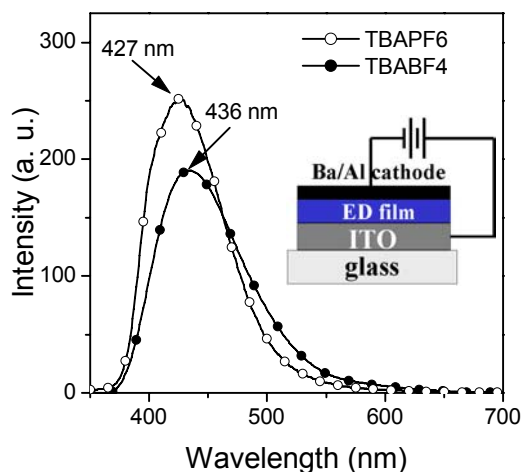


Figure S9. Normalized EL spectra of devices with structures of ITO/ED films /Ba/Al.

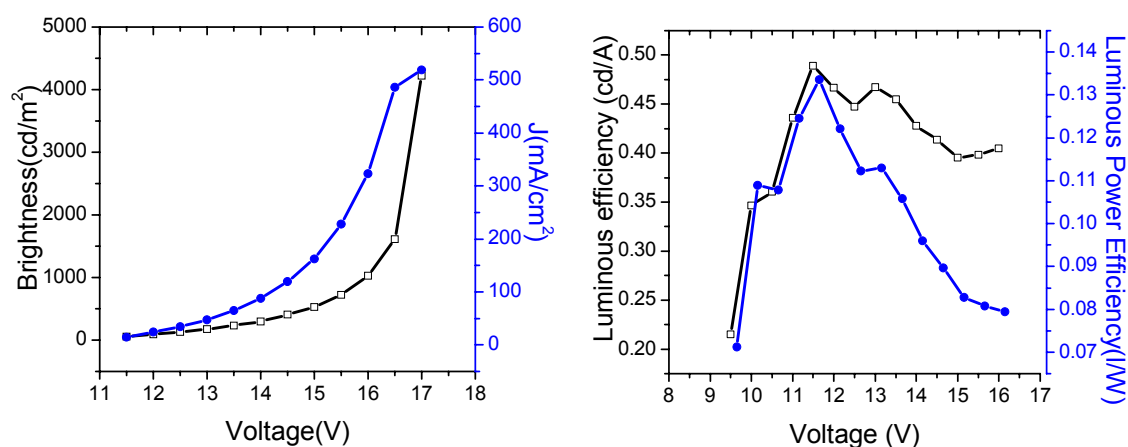


Figure S10. Relation between current density, luminance, efficiency and voltage of OLEDs with TCPC by ED films using TBAPF₆ as supporting electrolyte.

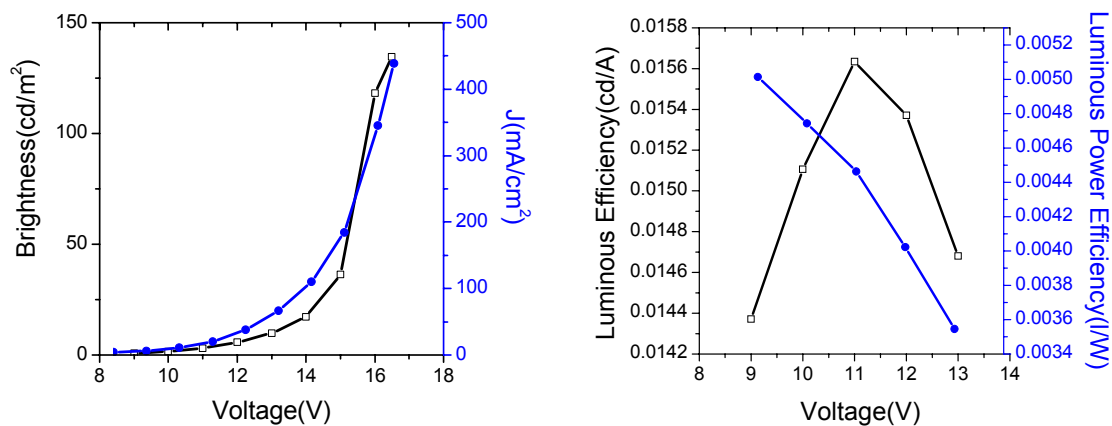


Figure S11. Relation between current density, luminance, efficiency and voltage of OLEDs with TCPC by ED films using TBABF₄ as supporting electrolyte.

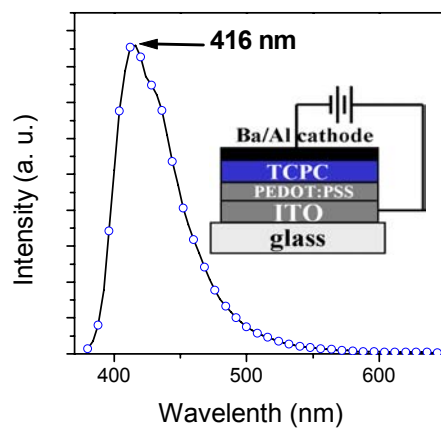


Figure S12. Normalized EL spectra of devices with structures of ITO/PEDOT:PSS/TCPC/Ba/Al.

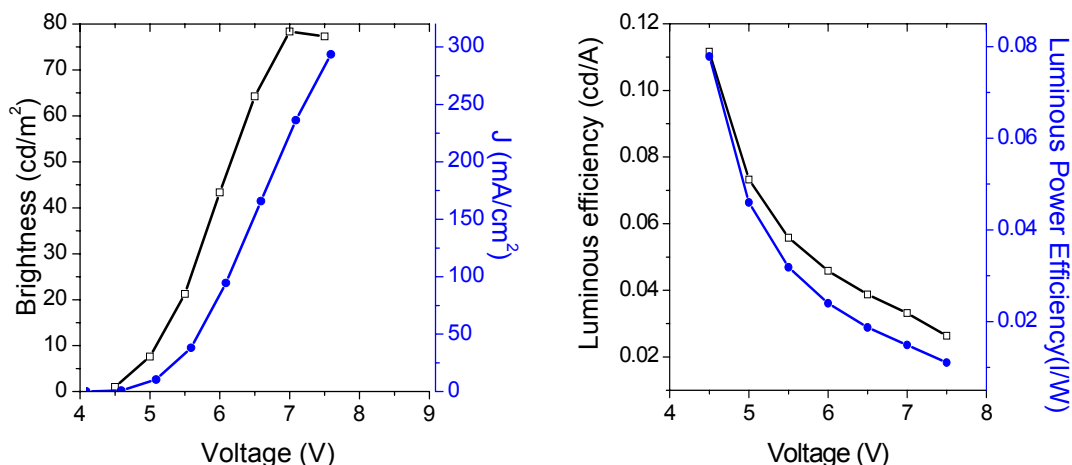


Figure S13. Relation between current density, luminance, efficiency and voltage of OLEDs with TCPC by spin-coating films as EL layer.

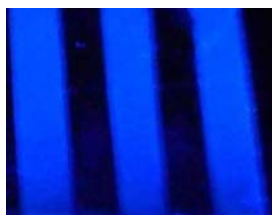


Figure S14. Fluorescence of the patterned ED film made under CV. The width of all patterned stria is 1 mm. For this experiment we have used 1.0 mg/mL TCPC/0.1 M TBAPF₆ solution in a mixture of acetonitrile and CH₂Cl₂ ($v/v = 3/2$). After ED process, the resulting ED film was then washed with acetonitrile to remove any unreacted precursors.

References

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