Supporting Information

Efficient Emissive Fluorene-based *p-n* Conjugated Porous Materials for Nearly White Electroluminescence: Benefit from Metal-free Friedel-Crafts Green Polymerization

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Supplementary Materials

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EXPERIMENTAL SECTION

Chemicals

All starting materials and reagents were obtained from commercial suppliers and used without further purification. Column chromatography was performed on silica gel 60 (0.040−0.063 mm). Tetrahydrofuran were dried and distilled from sodium/benzophenone， and dichloromethane were dried by Na_2SO_4. TPhOH and its two reactant were synthesized according to our previous work.[1]

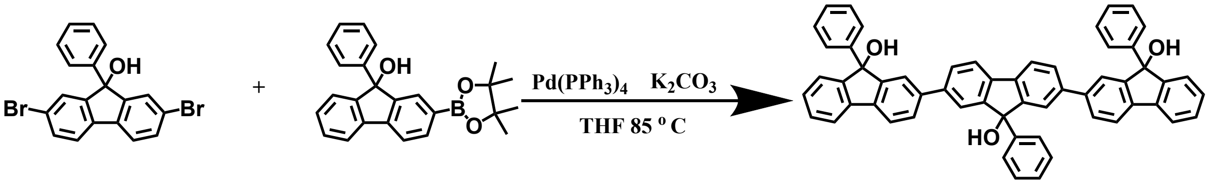
Materials and Characterization

FTIR were recorded using a Nicolet 20XB FT-IR spectrophotometer in 400−4000 cm^{-1}. Samples were prepared by dispersing the complexes in KBr to form disks. Solid-state ^{13}C CP-MAS spectrum was recorded on a Varian InfinityPlus 400 spectrometer at 100.61 MHz at an MAS rate of 10.0 kHz using zirconia rotors 4 mm in diameter using a contact time of 4.0 ms and a relaxation delay of 2.0 s. ^{1}H NMR was recorded on a Bruker 400 MHz spectromet spectrometer in $CDCl_3$, using tetramethylsilane (TMS) as the interval standard. XPS was recorded by Escalab250. Elemental analyses were determined with an Elementar Vario EL cube elemental analyzer. The measurements of Energy Dispersive Spectrometer (EDS) were performed on the SEM Hitachi, S-4800. BET testing were congducted by Surface Area and porosimetry Analyzer V-Sorb 2800p. The quantum yields of polymers were measured on an Edinburgh FLS-920 spectrometer. For scanning electron microscopic (SEM) studies, a drop of 20 μL solutions were placed onto silicon substrates, and the solvent was left to evaporate. The samples were then examined with a field emission SEM (Hitachi, S-4800) at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) images were obtained on a Hitachi operated at 100 kV. Absorption spectra were measured with a Shimadzu UV-3600 spectrometer at 25 °C, and emission spectra were recorded on a Shimadzu RF-5301(PC) luminescence spectrometer. The film morphologies of polymer films were recorded 5 μm multiply 5 μm with a Park AFM in tapping mode. Film thicknesses were measured using a

Bruker Dektak XT stylus profiler. The fluorescence lifetime were recorded on Edinburgh FLS-920 spectrometer by using 379 nm laser. Thermogravimetric analyses (TGA) were conducted by a Shimadzu DTG-60H under a heating rate of 10 °C/min and a nitrogen flow rate of 50 cm^3/min.

Preparation of 9,9,9-triphenyl-9H,9H,9H-[2,2:7,2-terfluorene]-9,9,9-triol (TPhOH):

2,7-dibromo-9-phenyl-9H-fluoren-9-ol (0.5 g), 9-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxabo -rolan-2-yl)-9H-fluoren-9-ol (1.38 g) and $Pd(PPh_3)_4$ (0.2 g) was added into dry two-necked flask (250 mL) under nitrogen. Then injecting K_2CO_3 (2 M 5 mL) and tetrahydrofuran (20 mL) into the flask. The mixture stir and refluxed 48h under 85 °C. After cooling the reaction room temperature, the mixture was extracted with distilled water and dichloromethane. The combined organic layer was dried with Na_2SO_4 and evaporated in a rotary evaporator. The residue was purified by column chromatography using petroleum ether: ethyl acetate=4:1 as eluent to afford TPhOH (0.64 g, 69%). The characterization data of TPhOH were obtained (Figure S3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (t, *J* = 8.0 Hz, 6H), 7.59 (t, *J* = 8.4 Hz, 4H), 7.53 (d, *J* = 2.3 Hz, 4H), 7.43 – 7.27 (m, 14H), 7.25 – 7.19 (m, 7H), 2.53 (d, *J* = 6.7 Hz, 1H), 2.48 (d, *J* = 6.9 Hz, 2H).



***Scheme S1.* Synthetic routes of TPhOH.**

Preparation of TPhOH-TCTA:

To a solution of TPhOH (0.25 g, 0.3 mmol) in anhydrous dichloromethane (20 mL), 2,4,6-trichloro-1,3,5-triazine (0.18 g, 0.98 mmol) and boron trifluoride diethyl etherate (0.4 mL) were added. After 4 hours, the reaction mixture was quenched by water and then the mixture was extracted with distilled water and dichloromethane. The combined organic layer was dried with Na_2SO_4 and evaporated in a rotary evaporator.

Further purification was done by soxhlet extraction with methanol and normal hexane, respectively. Finally, the product was dried at 333 K overnight to give a gray-white powder (75 % yield).

Device Fabrication:

The ITO-glass were ultrasonic cleaned sequentially with detergent, ethyl alcohol, acetone, and demonized water, then dried in an oven, then treated in an ultraviolet-ozone chamber for 5 min. PEDOT: PSS was spin-coated onto the ITO-glass at a speed of 3000 rpm for 60 s annealed then at 120 °C for 10 min. Next, the CPM dispersed in chloroform (10 mg/ml) were spin-coated on the film of PEDOT:PSS at a speed of 2000 rpm for 30 s and then transferred into the glovebox full of N_2 for annealing at 80 °C for 20 min. Finally, TPBi (20 nm), LiF (0.8 nm) and Al (100 nm) were deposited onto the active polymer layer successively using thermal evaporation in vacuum through a shadow mask under a base pressure of $\sim 4 \times 10^{-4}$ torr. The current-voltage luminescence characteristics of the devices were recorded using a combination of a Keithley source meter (model 2400) and a luminance meter. The EL spectra and CIE coordinates of the devices were analyzed with a spectra-scan PR765 spectrophotometer. All the devices were characterized without encapsulation, and all the measurements were carried out in the ambient condition at room temperature (R.T.). The emission area of the devices is 4 mm^2 as defined by the overlapping area of the ITO films and top electrodes.

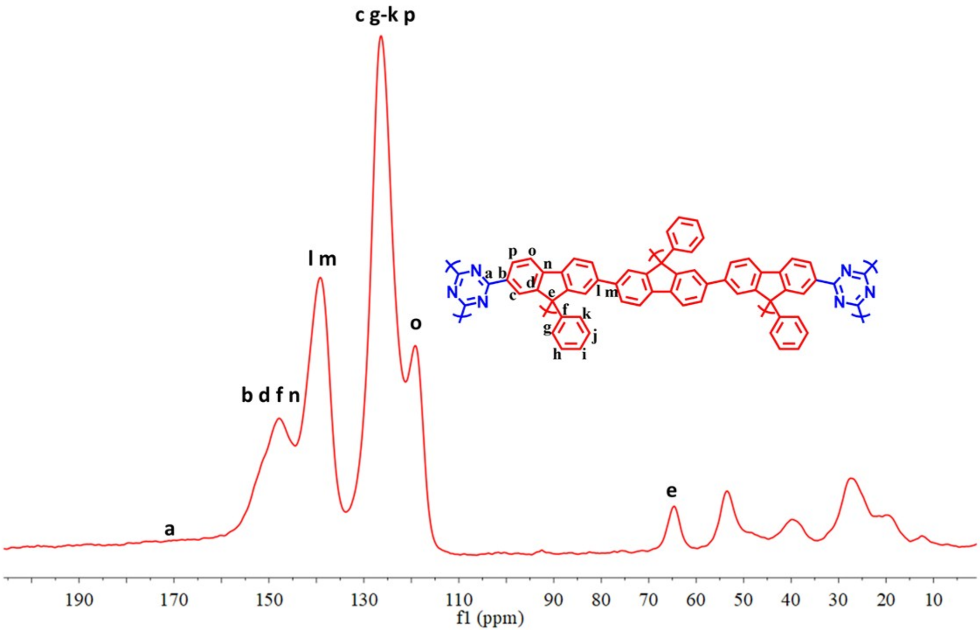
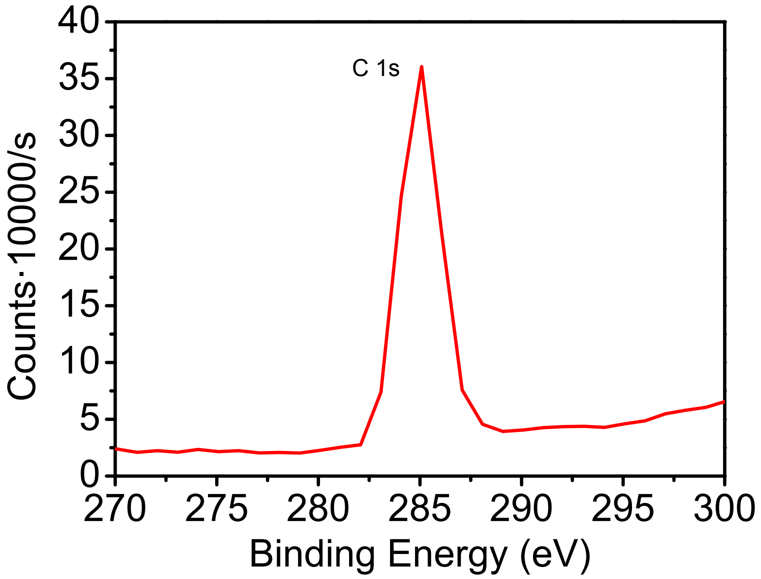


Figure S1. Solid states ^{13}C CP-MAS NMR spectra of TPhOH-TCTA.



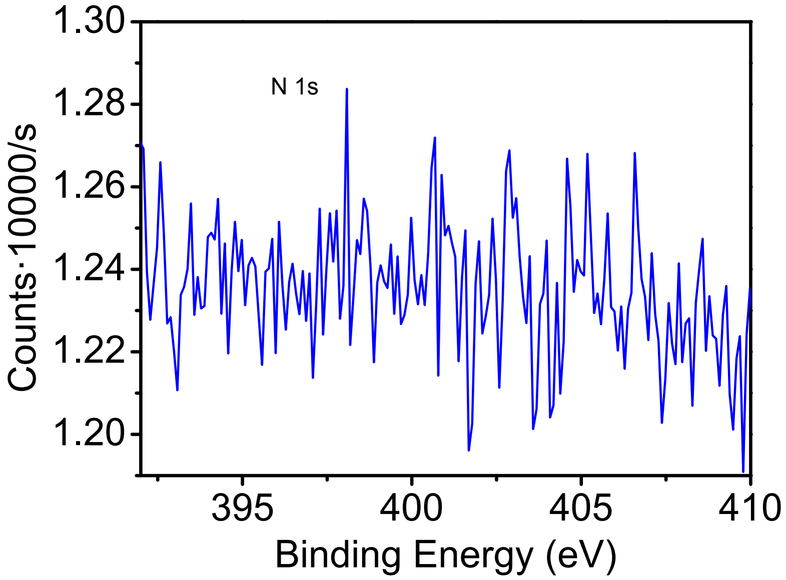


Figure S2. C 1s and N 1s XPS spectra of TPhOH-TCTA.

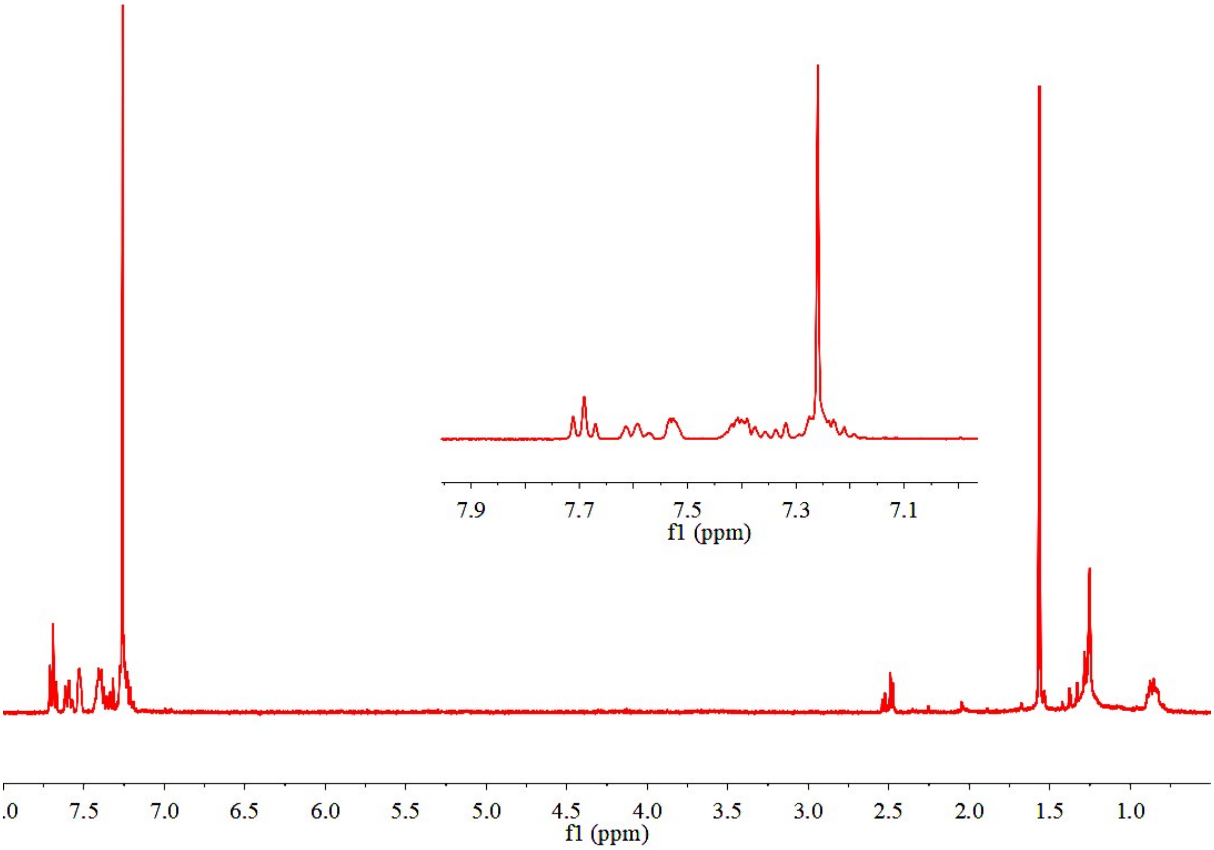


Figure S3. ^{1}H NMR spectra of TPhOH.

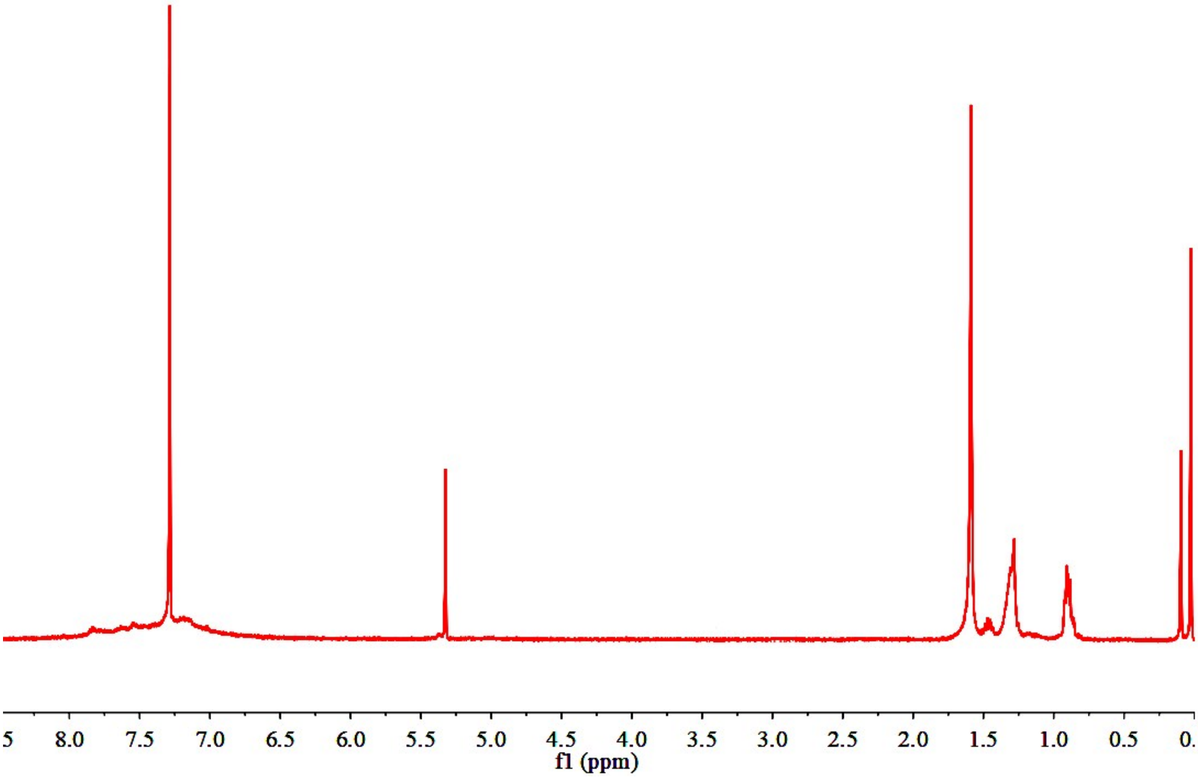


Figure S4. ^{1}H NMR spectra of TPhOH-TCTA.

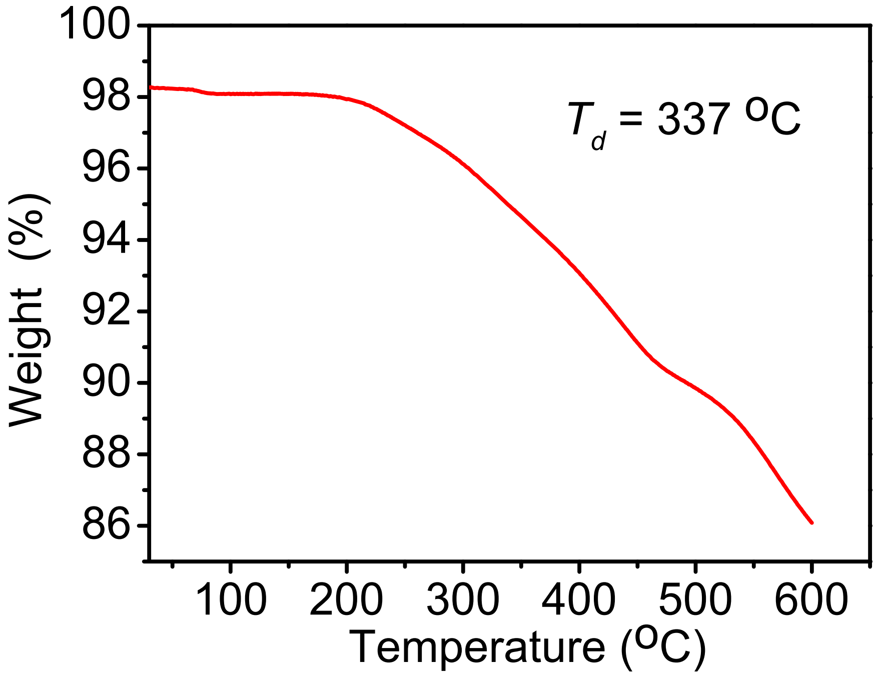


Figure S5. TGA curve of TPhOH-TCTA.

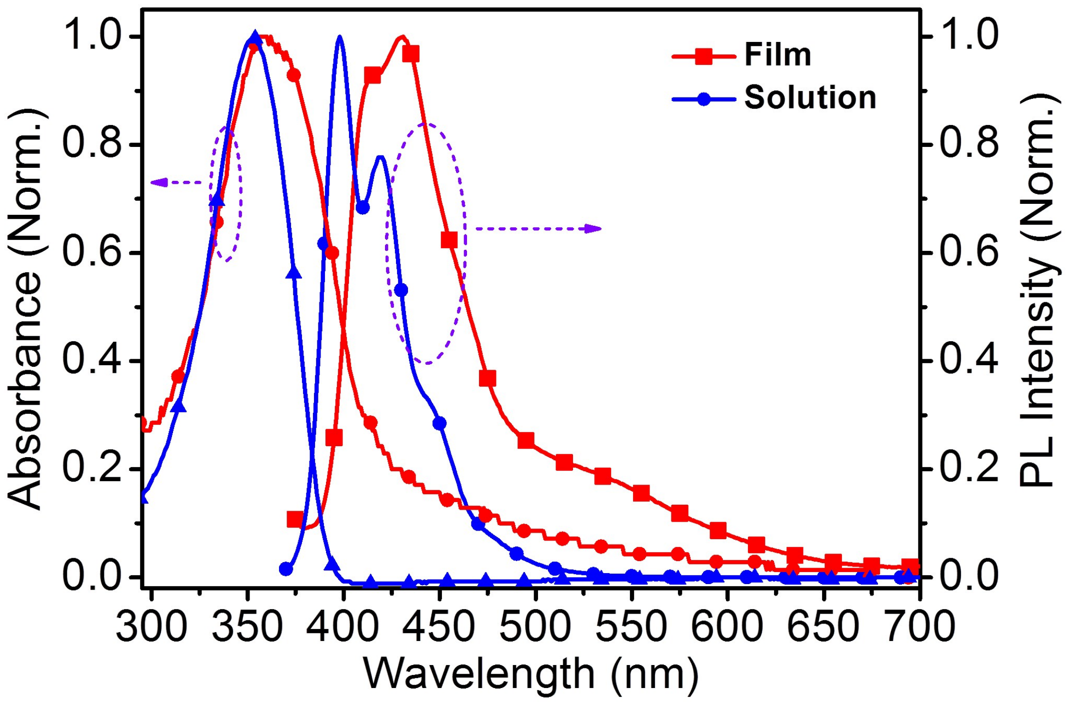


Figure S6. Absorption and emission spectra of TPhOH in various states.

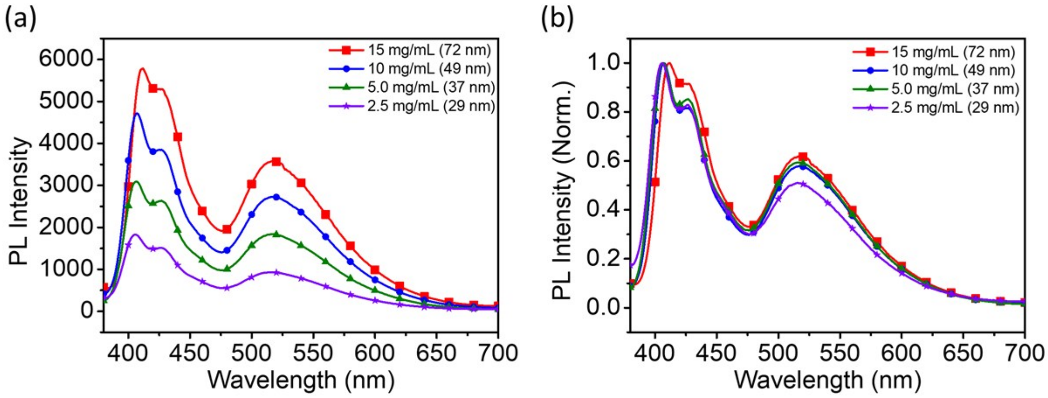


Figure S7. PL spectra of TPhOH-TCTA films spin-coated from different concentrations.

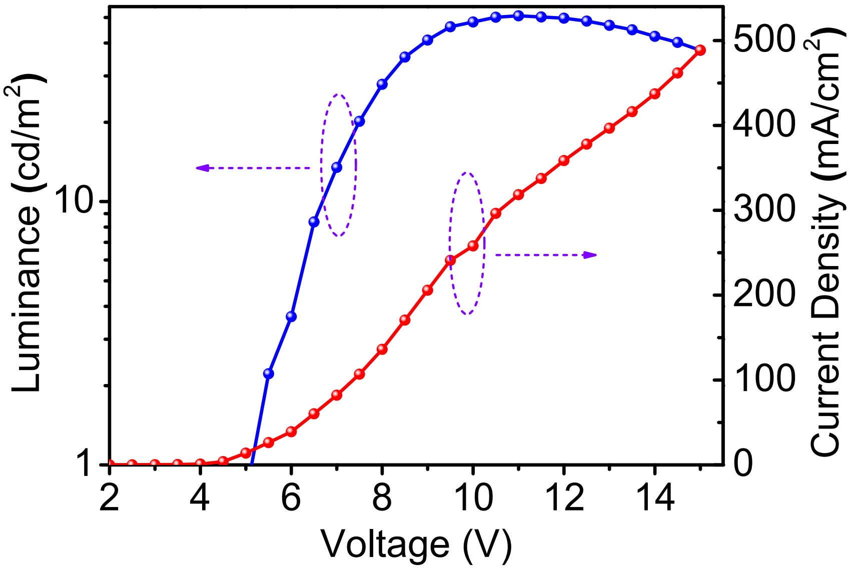


Figure S8. The graphic of Voltage – Luminance and Current Density of the device.

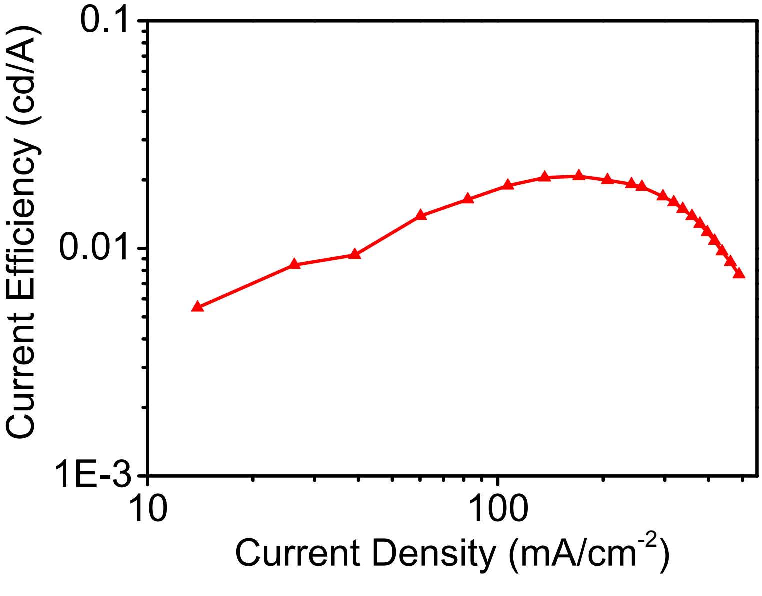


Figure S9. The graphic of Current Density and Current Efficiency of the device.

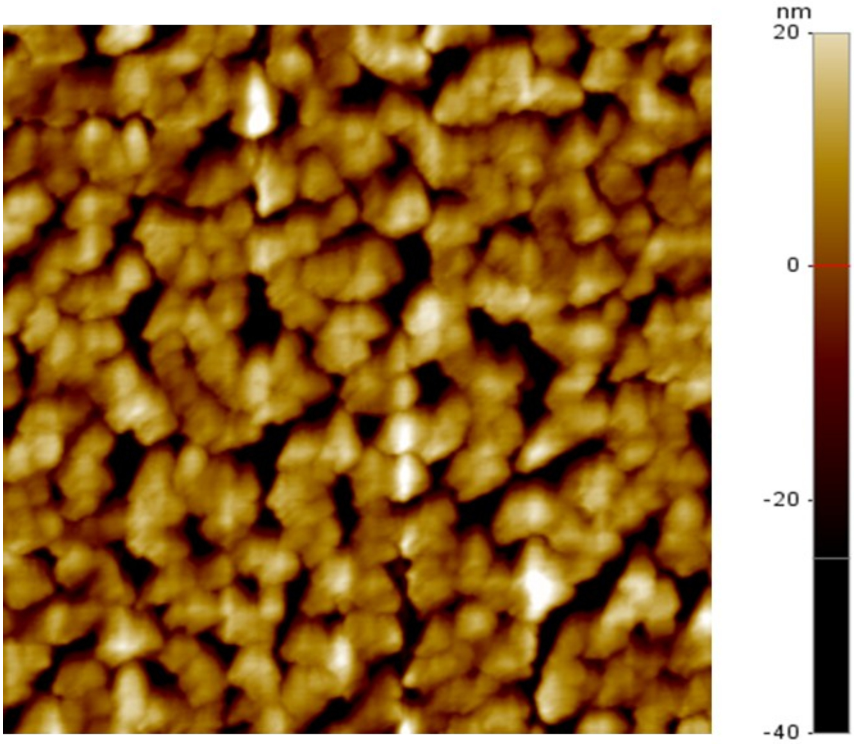


Figure S10. 2D AFM images of TPhOH-TCTA films spin-coated from $CHCl_3$ solution with the concentration of 10 mg/mL.

Table S1. The Porosity Parameters of TPhOH-TCTA.

Sample	S_{BET} ($m^2 g^{-1}$)	$S_{Langmuir}$ ($m^2 g^{-1}$)	S_{micro} ($m^2 g^{-1}$)	V_{micro} ($cm^3 g^{-1}$)	V_{total} ($cm^3 g^{-1}$)	Pore size (nm)
TPhOH-TCTA	**179**	**258**	**99**	**0.039**	**0.176**	**2.4 / 3.4 / 6.6**

[a]Microporous surface area calculated using the t-plot method. [b]Microporous volume calculated using the t-plot method. [c]Total porous volume calculated at P/P0 = 0.9899.

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