Supporting Information

Conductivity-Enhanced Thick Hole-Transporting Layers via Doping–Crosslink Synergy for Efficient and Stable NIR QLEDs

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Experimental

Materials: Formamidine acetate ($HN{=}CHNH_2{\cdot}CH_3COOH$, 99%, Sigma-Aldrich), Lead (II) iodide (PbI_2, 99%, Sigma-Aldrich), Oleylamine (OAm, technical grade 70%, Adamas), Oleic acid (OA, technical grade 90%, Sigma-Aldrich), 1-Octadecene (ODE, technical grade 90%, Adamas), Methyl acetate (ReagentPlus, 99%, Sigma-Aldrich). Octane (anhydrous, ⩾99%, Sigma-Aldrich). PEDOT:PSS solution (Clevios PVP AI 4083), Poly-TPD, and POT2T were purchased from Xi'an Polymer Light Technology Corp. 4,4'-bis (3-vinyl-9H -carbazol-9-yl)1,1'-biphenyl (CBP-V) was purchased from Sigma-Aldrich. All the chemicals were used directly as received.

$FAPbI_3$ PQDs: In a typical synthesis, 624 mg FAAC and 12 mL OA were dried in a 3-necked round bottom flask at room temperature for 15 min. The reaction mixture was degassed for 5 min at room temperature and was rapidly heated to 110℃ and continued to be degassed for 60 minutes. After the reaction forming a clear FA-oleate precursor solution, nitrogen (N_2) was introduced, and the temperature was kept at 100℃. Before hot injection, the system temperature of the FA-precursor was dropped to 80℃. In another flask, 350 mg PbI_2 was mixed with 2 mL of OAm/OA mixture and 20 mL of ODE followed by vacuum drying at 100℃ for 100 min. Under N_2 atmosphere, the lead halide precursors were kept at a reaction temperature of 80℃ until all solids were dissolved. Then, 4.0 mL FA-precursor solution was rapidly injected into the flask containing the lead halide precursor. The solution was then swiftly cooled using an ice water bath. The solution was centrifuged at 7800 rpm to remove unreacted precursors. The supernatant was discarded, and the precipitation was collected. Then dissolve the precipitate with octane to obtain $FAPbI_3$ crude PQDs solution. Methyl acetate was added to the crude PQDs solution. The mixture was then centrifuged to collect the precipitant and dissolve in the octane. This purification step was repeated. The collected precipitant was dissolved in the octane to obtain purified $FAPbI_3$ solution. The PQDs solution was stored at 4 ℃ until further use.

Fabrication of Devices:

Before spin-coating and blade-coating, the ITO substrate was cleaned in acetone, ethanol, and deionized water for 15 min each.

Spin-coating:

PEDOT:PSS (0.45 μm filtered) was drop-cast in air, spin-coated at 4000 rpm for 60 s, and annealed at 150 °C for 15 min; substrates were then transferred to a N_2 glovebox. Poly-TPD (8 mg mL^{-1} in chlorobenzene, 0.22 μm filtered) was spin-coated at 3000 rpm for 40 s and annealed at 120 °C for 20 min. CBP-V and CBP-V:TAPC: CBP-V (10, 20, and 30 mg mL^{-1} in chlorobenzene) or CBP-V:TAPC (TAPC doping concentration: 20 wt%, 33 wt%, 50 wt%, and 66 wt%, 30 mg mL^{-1} in octane) solutions were filtered, spin-coated at 3000 rpm for 40 s, annealed at 150 °C for 30 min, and immediately UV-exposed (365 nm, ~10 mW cm^{-2}) for 30 min. QDs (20 mg mL^{-1} in octane) were spin-coated at 3000 rpm for 40 s without further annealing. Finally, ~60 nm of POT2T, ~2 nm of Liq, and ~100 nm of Al were deposited using a thermal evaporation system at a pressure below 4×10^{-4} Pa.

Blade-coating:

The PEDOT:PSS was dropped onto the ITO substrate preheated to 50 ℃. The solution was spread using a blade with a gap of 200 μm at a speed of 20 mm s^{-1}. The PEDOT:PSS film was then annealed at 150 ℃ for 15 min. Subsequent layers of Poly-TPD (10 mg mL^{-1} in chlorobenzene) CBP-V(10, 20, and 30 mg mL^{-1} in chlorobenzene) and CBP-V:TAPC (TAPC doping concentration: 20 wt%, 33 wt%, 50 wt%, and 66 wt%, 30 mg mL^{-1} in octane) were blade-coated with gaps of 250 μm, respectively. Then, Poly-TPD was annealed at 120 ℃ for 10min. CBP-V and CBP-V:TAPC were annealed at 150 °C for 30 min, followed by immediate UV exposure (365 nm, ~10 mW cm^{-2}) for 30 min. QDs (20 mg mL^{-1} in octane) were blade-coated with gaps of 300 μm without further annealing. Finally, ~60 nm of POT2T, ~2 nm of Liq, and ~100 nm of Al were deposited using a

thermal evaporation system at a pressure below 4×10^{-4} Pa.

Characterizations: UV-Vis absorption spectra were measured by a Shimadzu UV-3600PC scanning spectrophotometer. The photoluminescence (PL) spectra were collected by a fluorescence spectrometer (QUANTAURUS-Tau). The FTIR spectra were measured by VERTEX 70 FT-IR Spectrometer under transmission mode. The contact angle was measured using a DataPhysics OCA system. Atomic force microscope (AFM) images were captured with a Bruker Dimension ICON. Work functions were determined using ultraviolet photoelectron spectroscopy (Ultra DLD). Electroluminescence (EL) spectra, current density-voltage-luminance (J-V-L) characteristics, and external quantum efficiency (EQE) was measured using a PR 745 photometer combined with a Keithley 2400 Source Meter.

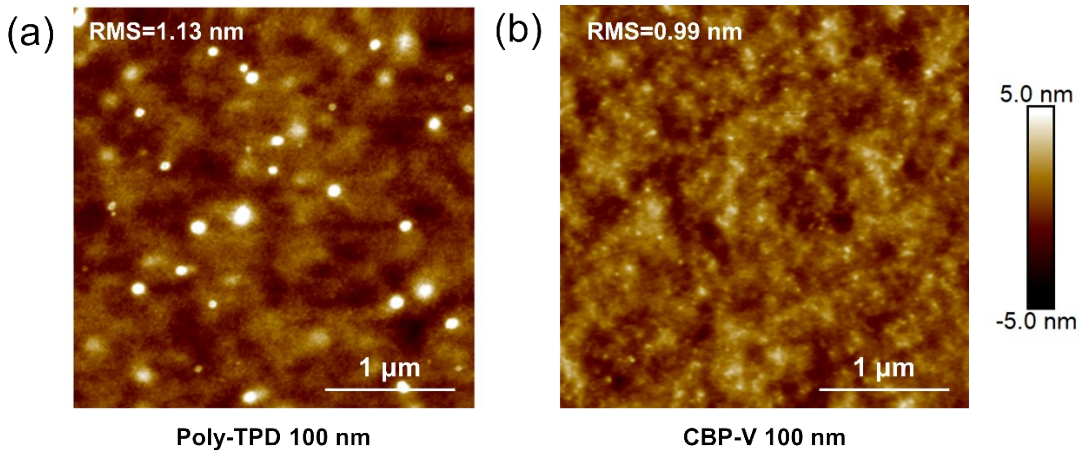

Fig. S1. AFM images of 100 nm-thick films: (a) Poly-TPD; (b) CBP-V.

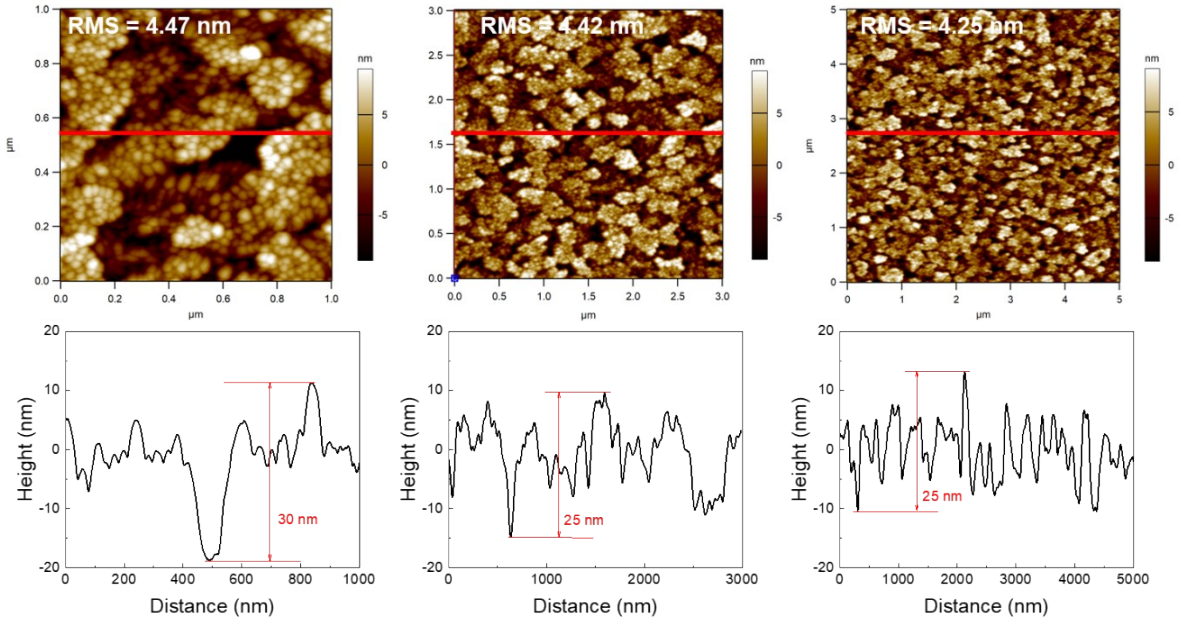

Fig. S2. AFM images of ITO.

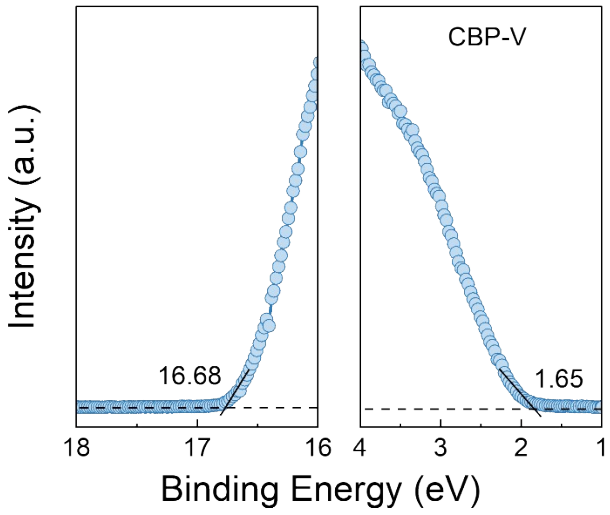

Fig. S3. UPS spectra of CBP-V.

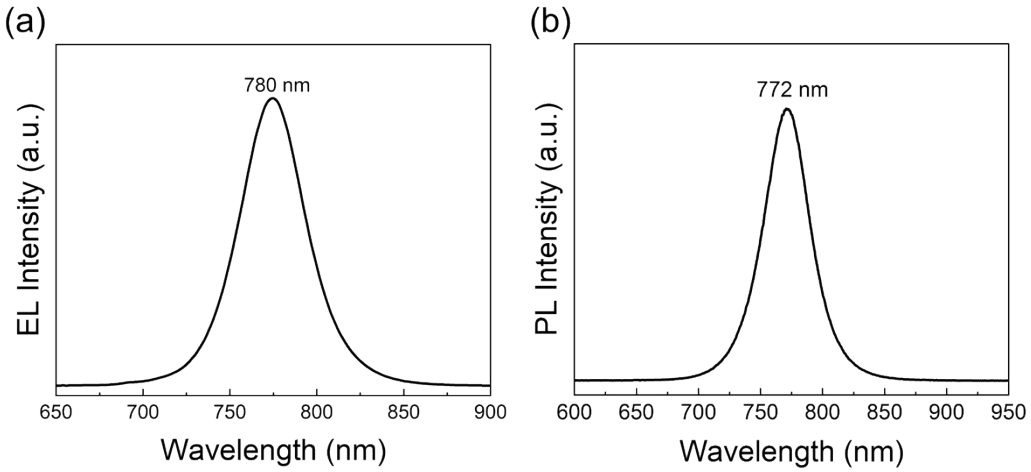

Fig. S4. (a) EL spectrum of the CBP-V device; (b) PL spectrum of the $FAPbI_3$ quantum dots solution.

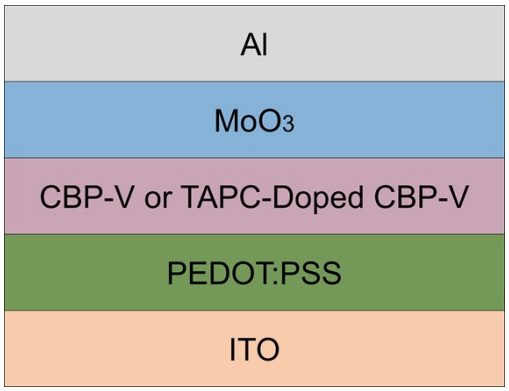

Fig. S5. Schematic diagram of the HOD structure.

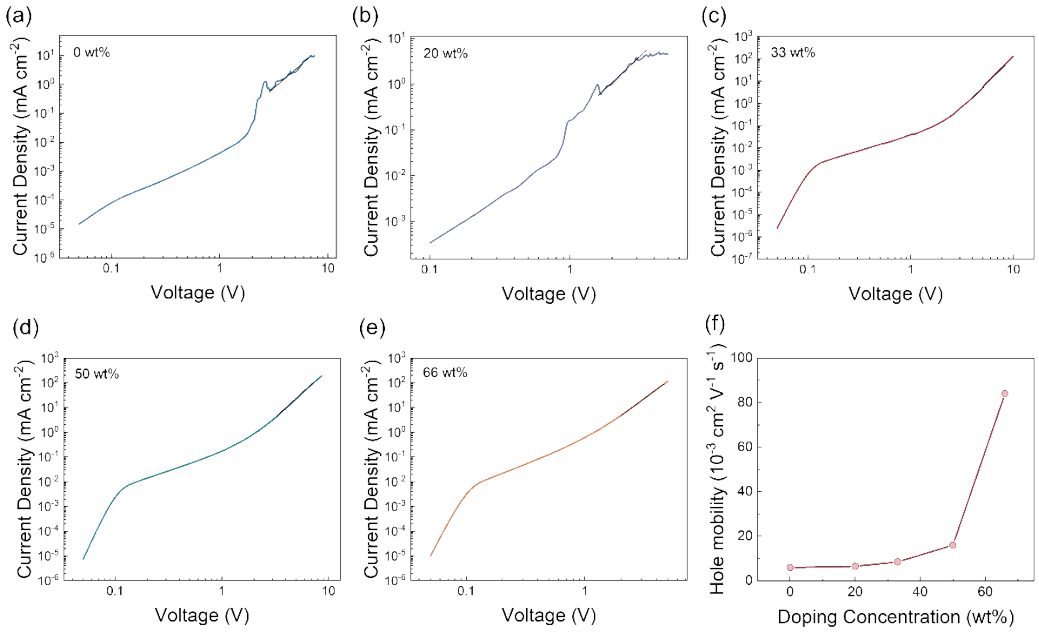

Fig. S6. J-V characteristics for HOD with doping concentrations of (a) 0 wt%,(b) 20 wt%,(c) 33 wt%,(d) 50 wt%, and (e) 66 wt%. The black line is the fitting curve; (f) Hole mobility statistics based on different doping concentrations of TAPC.

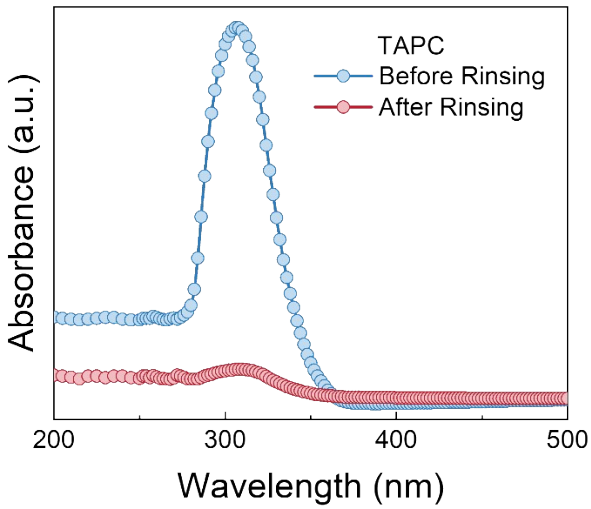

Fig. S7. UV-Vis spectra of the TAPC film before and after rinsing.

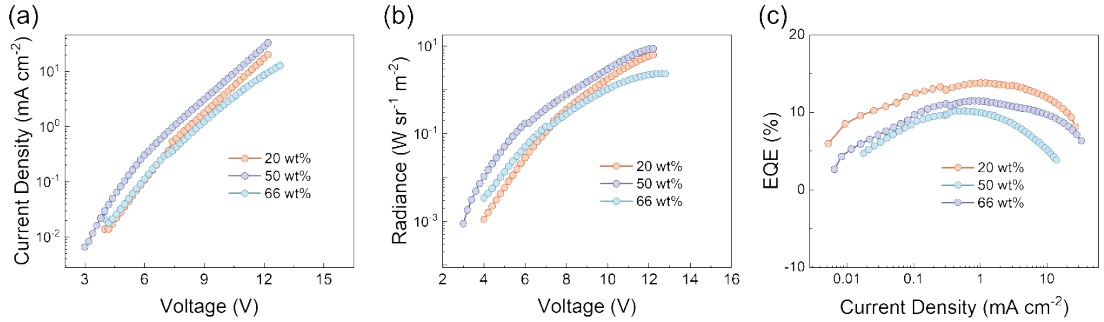

Fig. S8. J–V (a), J–R (b), and EQE–J (c) characteristics of QLEDs based on TAPC-doped CBP-V HTLs with different TAPC doping ratios.

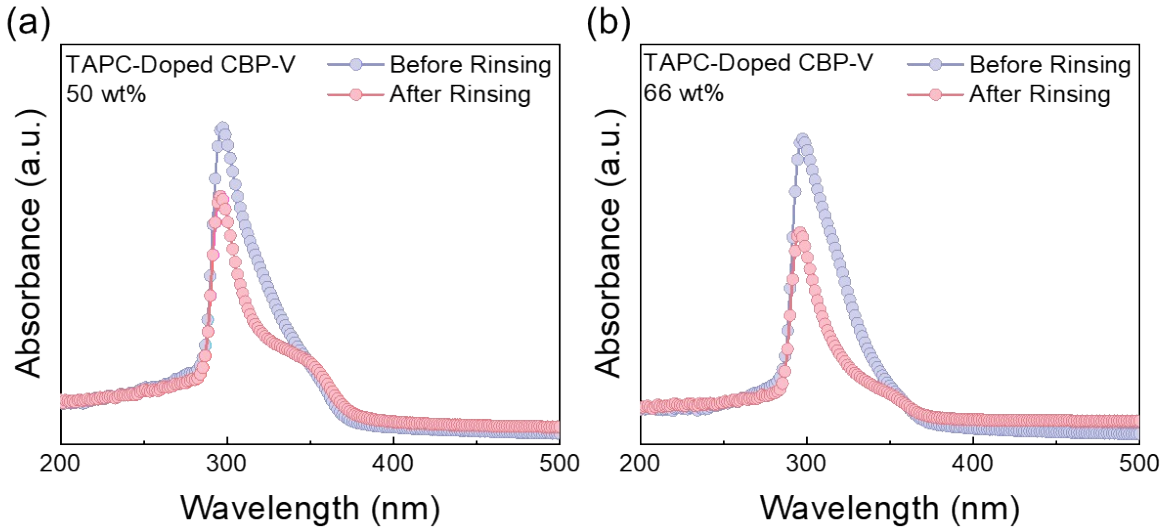

Fig. S9. UV-Vis spectra of the TAPC-doped CBP-V(50 wt%) (a) and TAPC-doped CBP-V(66 wt%) (b) films before and after rinsing.

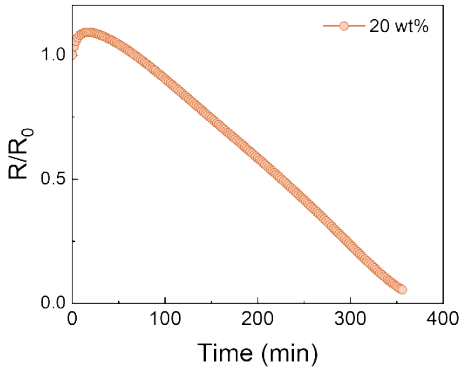

Fig. S10. Operational stability of QLEDs based on TAPC-doped(22 wt%) CBP-V HTLs.

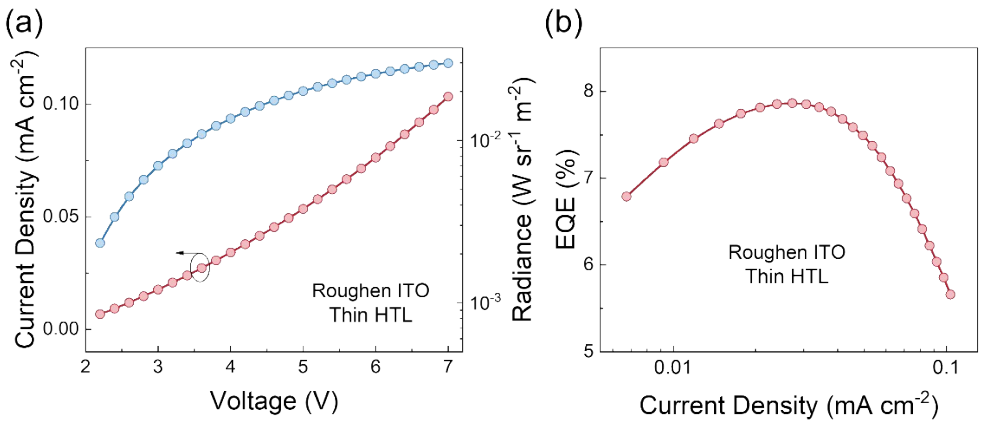

Fig. S11. Performance curves of the device with a thin HTL on hand-polished ITO: (a) J-V-R curve; (b) EQE-J curve.

Table S1 Thickness of CBP-V solutions with different concentrations.

Condition	Thickness (nm)			Average Thickness (nm)
10 mg mL^{-1}	21.80	22.28	22.48	22.19
30 mg mL^{-1}	104.19	105.70	105.84	105.24

Table S2 SCLC fitting slope and hole mobility based on different doping concentrations of TAPC.

TAPC Doping ratio	Slope	Hole mobility (cm^2 V^{-1} s^{-1})
0 wt%	0.177	5.9×10^{-4}
20 wt%	0.195	6.5×10^{-4}
33 wt%	1.254	8.5×10^{-4}
50 wt%	0.494	1.6×10^{-3}
66 wt%	2.511	8.4×10^{-3}