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Improved fullerene-free polymer solar cells using rationally designed mixed binary solution of electron extracting layer

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Materials and Instruments: All reagents were purchased from Sigma-Aldrich, Acros, Alfa, unless specified and used as received. The polymer PBDBT, and IITIC-Th were purchased from One Material. Alq3 bought from Alfa Company (Taiwan) and QPPBr purchased from Acros. PEDOT:PSS (Baytron Clevios P VP AI 4083, Germany) was obtained from Heraeus Group. Ultraviolet photoelectron spectroscopy (UPS) experiments were performed on a Thermo Scientific ESCALab 250Xi spectrometer. The gas discharge lamp was used for UPS, with helium gas admitted and the He I (21.22eV) emission line employed. The helium pressure in the analysis chamber during analysis was about $2E^{-8}$ mbar. The data were acquired with −10V bias. Absorption spectra were measured on a Hitachi U-3010 UV−vis spectrophotometer and carried out at room temperature. The thickness of the solid films was measured using a Dektak Profilometer. AFM images were measured using bruker multimode 8.0 atop the surface of the optimal solar cell devices.

Sample preparations and characterizations: Film samples for measurements of absorption mixed PBDBT:ITIC-Th, Alq3 and QPhPBr were prepared atop of the silica substrate via the spin-coating method. For the experiments of UPS of the electron transporting layers (ETLs), the ETL was spin-coated atop the clear Al surface. The HOMO level of QPhPBr and Alq3 was determined using ultraviolet photoelectron spectroscopy (UPS) with the incident photon energy, hv = 21.22 eV. The HOMO energy is calculated with the equation $E_{HOMO} = E_{cutoff} - E_{onset} - hv$, E_{cutoff}, and the E_{onset} are got from the UPS data.

Table S1. Summarize device performance of PBDBT:ITIC-Th based OSCs with different weight ratios of binary mixture of Alq3:QPhPBr ETL.

ETL	**V_{oc} (V)**	**J_{sc} (mA/cm^2)**	**FF (%)**	**PCE (%)**
1:0.5	0.84	16.88	59.78	8.47
1:1	0.84	17.45	62.45	9.15
1:1.5	**0.86**	**19.01**	**67.44**	**11.02**
1:2	0.83	18.55	65.95	10.15

Table S2. Different thickness of Binary Alq3:QPhPBr CBL fabrication study

ETL	**Thickness (nm)**	**V_{oc} (V)**	**J_{sc} (mA/cm^2)**	**FF (%)**	**PCE (%)**
Alq3:QPhPBr	5	0.848	17.61	65.15	9.73
Alq3:QPhPBr	8	0.851	18.57	67.10	10.60
Alq3:QPhPBr	**12**	**0.860**	**19.01**	**67.44**	**11.02**
Alq3:QPhPBr	15	0.859	18.28	66.38	10.42
Alq3:QPhPBr	19	0.854	17.74	64.92	9.83

Figure S1. UPS spectra of the onset (inset) and the secondary edge region of Alq3 and QPhPBr

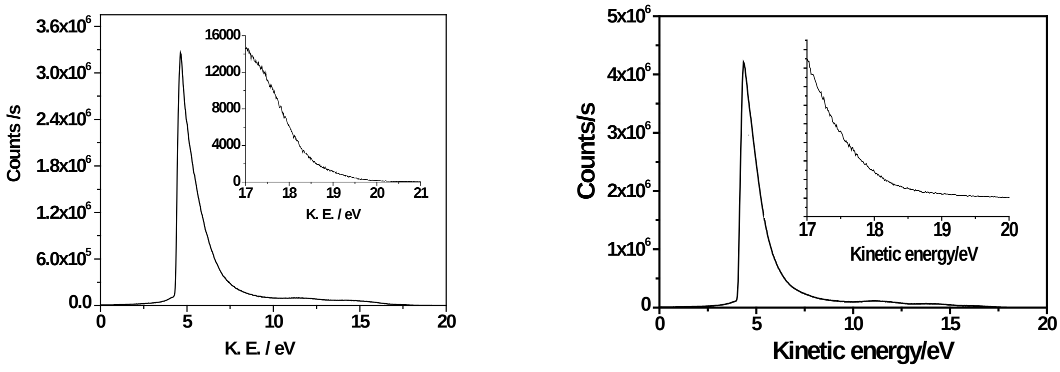


Table S3. UPS data for Alq3, QPhPBr, Alq3:QPhPBr measured from instrument and calculated work function

Name	**E_{fermi} (eV)**	**E_{cutoff} (eV)**	**WF (ϕ)**
Bare Al	21.11	4.14	4.25
Alq3	21.11	3.49	3.60
QPhPBr	21.11	3.95	4.06
Alq3:QPhPBr	21.11	3.85	3.96

Table S4. HOMO and LUMO energy of Alq3 and QPhPBr.

ETL	**λ_{onset} (nm)**	**Band Gap (eV)**	**HOMO (eV)**	**LUMO (eV)**
Alq3	441	2.86	-5.81	-2.95
QPhPBr	298	4.19	-6.77	-2.58

Measurements of electron mobility by the space-charge limited current (SCLC) method: The electron-only devices were fabricated with a configuration of ITO/titanium (diisopropoxide) bis(2,4-pentanedionate) (TIPD)/blend/ETL/Al. The TIPD buffer layer was prepared by spin-coating a 3.5 wt % TIPD isopropanol solution onto the pre-cleaned ITO substrate and then baked at 150 °C for 10 min to convert TIPD into TOPD. [S1] Subsequently, the blend was spin-coated on it under the same condition as preparation of the optimal solar cell. The Al layer was thermally deposited on the top of the blend in vacuum. The Al layer was deposited at a speed of 1 Å/ s. The electron mobility was extracted by fitting the current density–voltage curves using the Mott–Gurney law, [S2,S3] Equation (1) $J_{SCL}= 9\varepsilon\varepsilon_0\mu V^2 /(8L^3)$ (1) where ε is the dielectric constant of the organic component, ε_0 is the permittivity of the vacuum (8.85419×10^{-12} $CV^{-1}m^{-1}$), μ is the zero-field mobility, J is the current density, L is the thickness of the active layer, and $V = V_{app} - V_{bi}$, here V_{app} is the applied potential, and

V_{bi} the built-in potential which results from the difference in the work function values of the cathode (in the electron-only device, V_{bi} = 0.4 V). The electron mobility of the solar cell blend are deduced from the intercept value of $9\varepsilon\varepsilon_0\mu/(8L^3)$ by linearly plotting ln(J) vs. ln(V) (the slope of ln(J) vs. ln(V) is ≈ 2). The plot was presented in main manuscript.

Measurements of the hole mobility by the space-charge limited current (SCLC) method:

The devices were fabricated with configuration of ITO / PEDOT: PSS / PBDBT:ITIC-Th (200 nm) /Au. The Au layer was deposited under a low speed (1 Å/10 s) to avoid the penetration of Au atoms into the active layer. The active layers were spin-coated with chlorobenzebe (CB) and dried. The hole mobility extracted by fitting the current density–voltage curves using the Mott–Gurney law.[S2,S3]

$$J_{SCL} = 9\varepsilon\varepsilon_0\mu V^2/(8L^3) \qquad (1)$$

where ε is the dielectric constant of the organic component, ε_0 is the permittivity of the vacuum (8.85419×10^{-12} $CV^{-1}m^{-1}$), μ is the zero-field mobility, J is the current density, L is the thickness of the active layer, and V_{bi} the built-in potential which results from the difference in the work function of the anode and the cathode (in this device structure, V_{bi} = 0.2 V). Herein ε is 3. The results are shown in Figure S2. The hole mobility of the solar cell blend are deduced from the intercept value of $9\varepsilon\varepsilon_0\mu/(8L^3)$ by linearly plotting ln(J) vs. ln(V) (the slope of ln(J) vs. ln(V) is ≈ 2) and calculated value as 1.59×10^{-4} cm^2 V^{-1} s^{-1}.

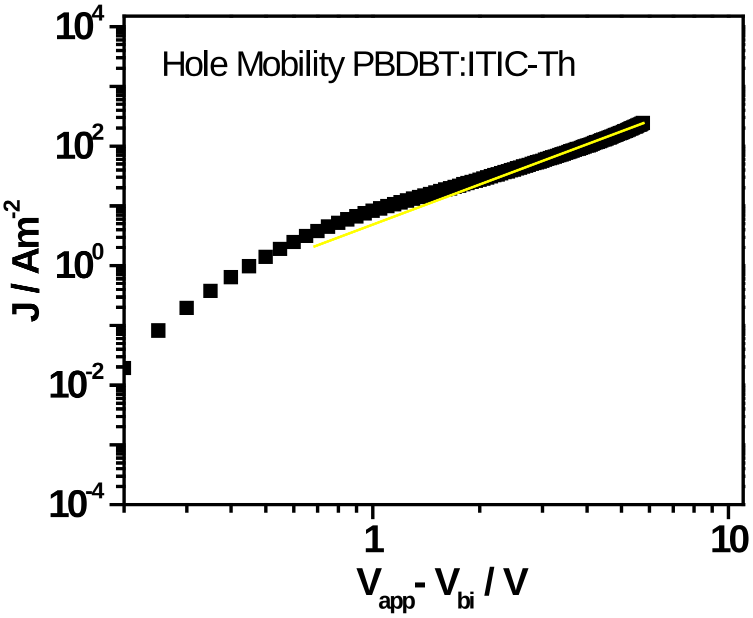
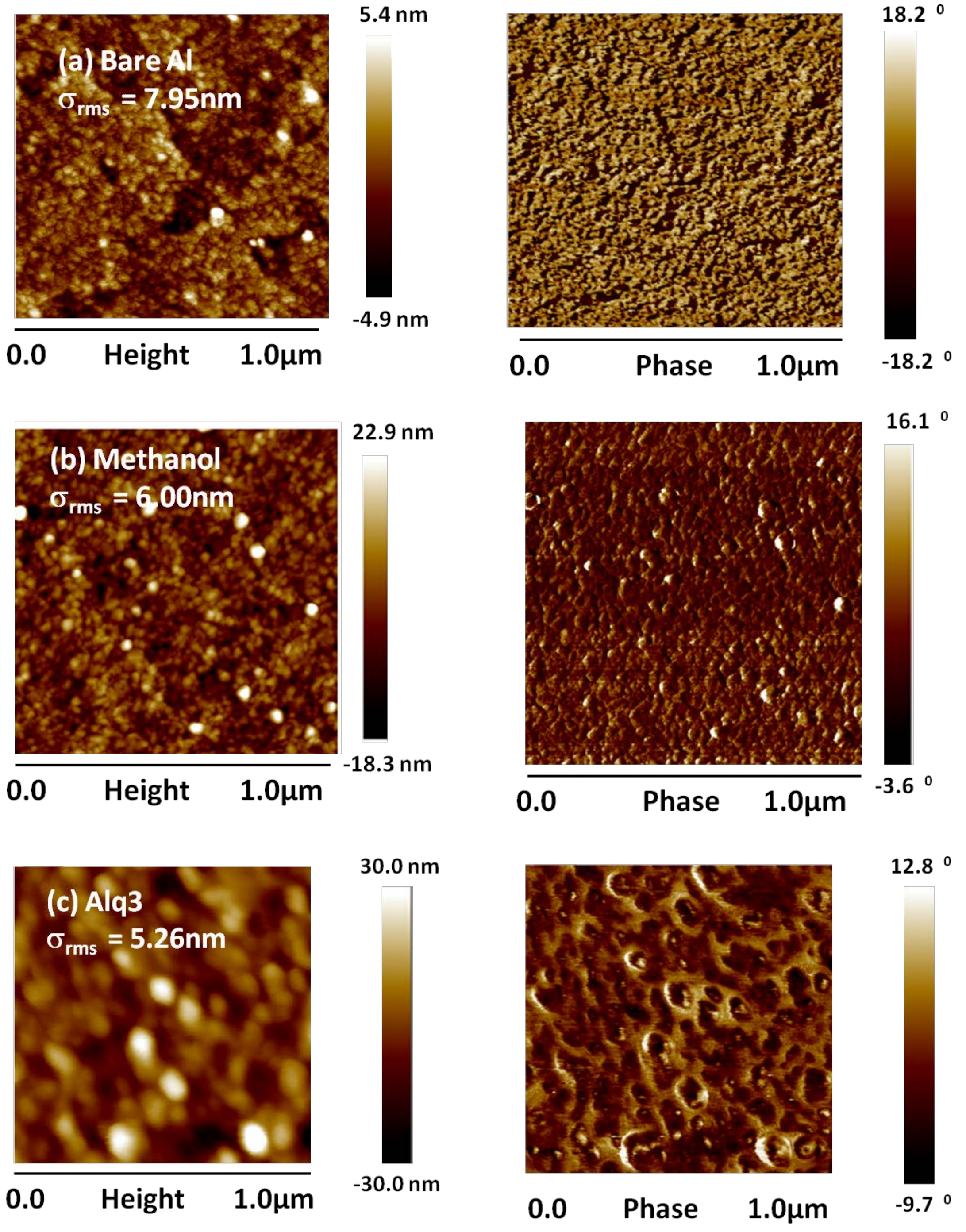


Figure S2 Plots of J–V obtained from PBDBT:ITIC-Th based hole only device, which were estimated using the SCLC method.

AFM Measurement: To understand morphological features affect using different CBL condition AFM height and phase images of blend active layer PBDB-T:ITIC were demonstrated and presented in Figure S3. AFM study reveals morphological properties which influenced by organic–metal contact, charge transport, and optical property significantly. Control device without CBL indicates 7.95nm surface roughness defined the morphological characteristics of photoactive layer. After treatment of methanol solvent over active layer roughness reduced to 6.00nm. In presence of Alq3 as ETL the surface roughness was measured as 5.26nm shows that too high roughness causes bad conducting effect on surface morphology. However after insertion of QPhPBr and mixed binary layer of Alq3:QPhPBr more reduction in roughness at 4.12nm and 3.95nm were observed, respectively. Significant change in roughness property of surface morphology about 4 nm from control device to dual mixture ETLs indicated that binary blend ETL have better tendency to provide moderate roughness quality reflected in its superior solar cell device performance. These results indicate that more reduction in surface roughness may significantly improve device performance and improves organic-metal contacts for better charge transport.



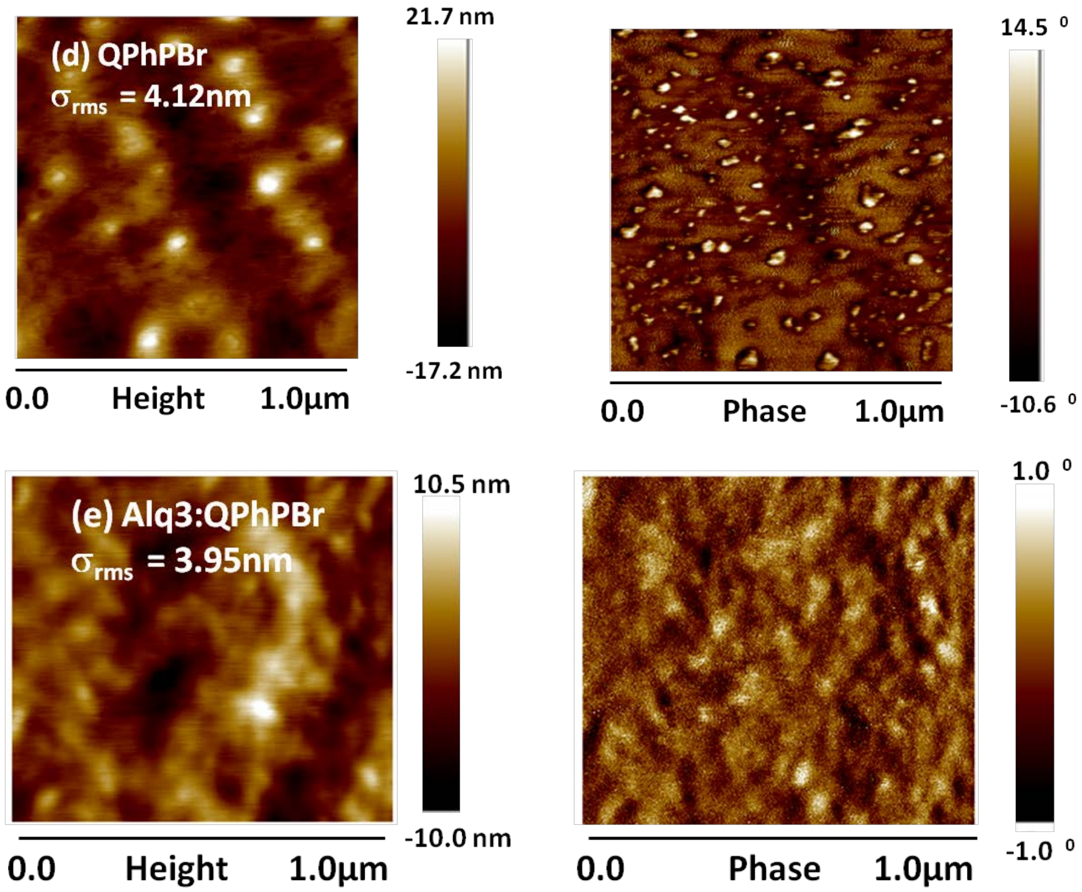


Figure S3 AFM Images of Different Coating Condition of ETL on PBDB-T:ITIC-Th Blend Active Layer Based Device.

References:

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