

Organic Hole Transport Materials for High Performance PbS Quantum Dot Solar Cells

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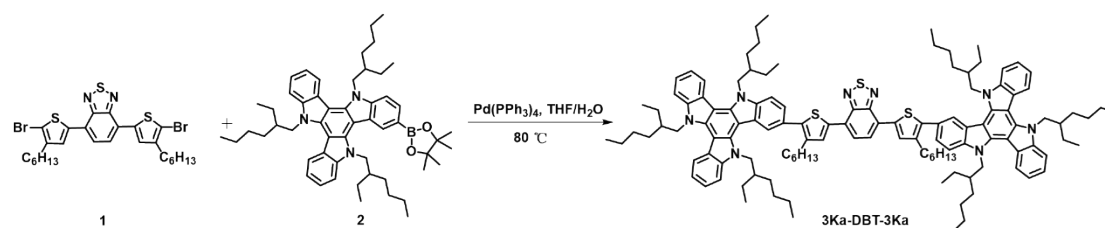
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Experimental section

1. General methods for synthesis

All the reactions were performed under nitrogen atmosphere unless mentioned. Almost all of the structures of the compounds were identified by ^1H NMR, ^{13}C NMR MS, and elemental analysis.

Synthetic procedures



Compounds 1 and 2 were synthesized by following the cited literature procedures^[1-3].

Synthesis of target compound

Compound 1 (1 g, 1.6 mmol), compound 2 (646 mg, 0.8 mmol), K_2CO_3 (332 mg, 2.4 mmol), $\text{Pd}(\text{PPh}_3)_4$ (20 mg/mmol) were dissolved in THF/ H_2O (5:1, v/v) under nitrogen atmosphere, the mixture was refluxed for 12 h. When the reaction was cooled to the room temperature, water washing and the mixture was extracted by CH_2Cl_2 . The combined organic phase was dried by anhydrous MgSO_4 and solution was removed by rotary evaporation. The crude product (900 mg, 70% yield) was purified by silica gel column chromatography and dried in vacuum. ^1H NMR (400 MHz, CDCl_3) δ 8.44 (s, 1H), 8.31 (s, 3H), 8.16 (s, 1H), 7.63 (t, $J = 9.5$ Hz, 6H), 7.48 – 7.30 (m, 7H), 4.99 (s, 9H), 2.89 (s, 3H), 1.88–1.67 (m, 3H), 1.14–0.79 (m, 48H), 0.73–0.60 (m, 18H), 0.57–0.43 (m, 16H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.57, 152.84, 152.84, 152.84, 141.09, 141.09, 139.56, 139.21, 130.19, 125.66, 125.56, 124.93, 123.75, 122.19, 122.19, 119.53, 119.53, 111.59, 111.49, 111.49, 111.43, 111.15, 109.54, 107.12, 107.04, 104.09, 103.86, 103.58, 103.52, 103.17, 103.00, 102.62, 97.23, 94.27, 50.76, 50.63, 50.17, 38.06, 37.99, 31.82, 31.77, 31.16, 29.85, 29.48, 29.27, 29.08, 28.25, 22.82, 22.74, 22.67, 14.16, 14.11, 13.90, 10.24, 10.17, 10.08, 9.97, 1.05, 0.02. MS (MALDI-TOF) m/z calculated for $\text{C}_{122}\text{H}_{154}\text{N}_8\text{S}_3$: 1828.1492; found, 1828.5530. Elem. Anal. (mass ratio, %) for 3Ka-DBT-3Ka ($\text{C}_{122}\text{H}_{154}\text{N}_8\text{S}_3$): C, 78.64 (80.12); H, 7.33 (8.39); N,

6.04 (6.68); S, 4.97 (5.25).

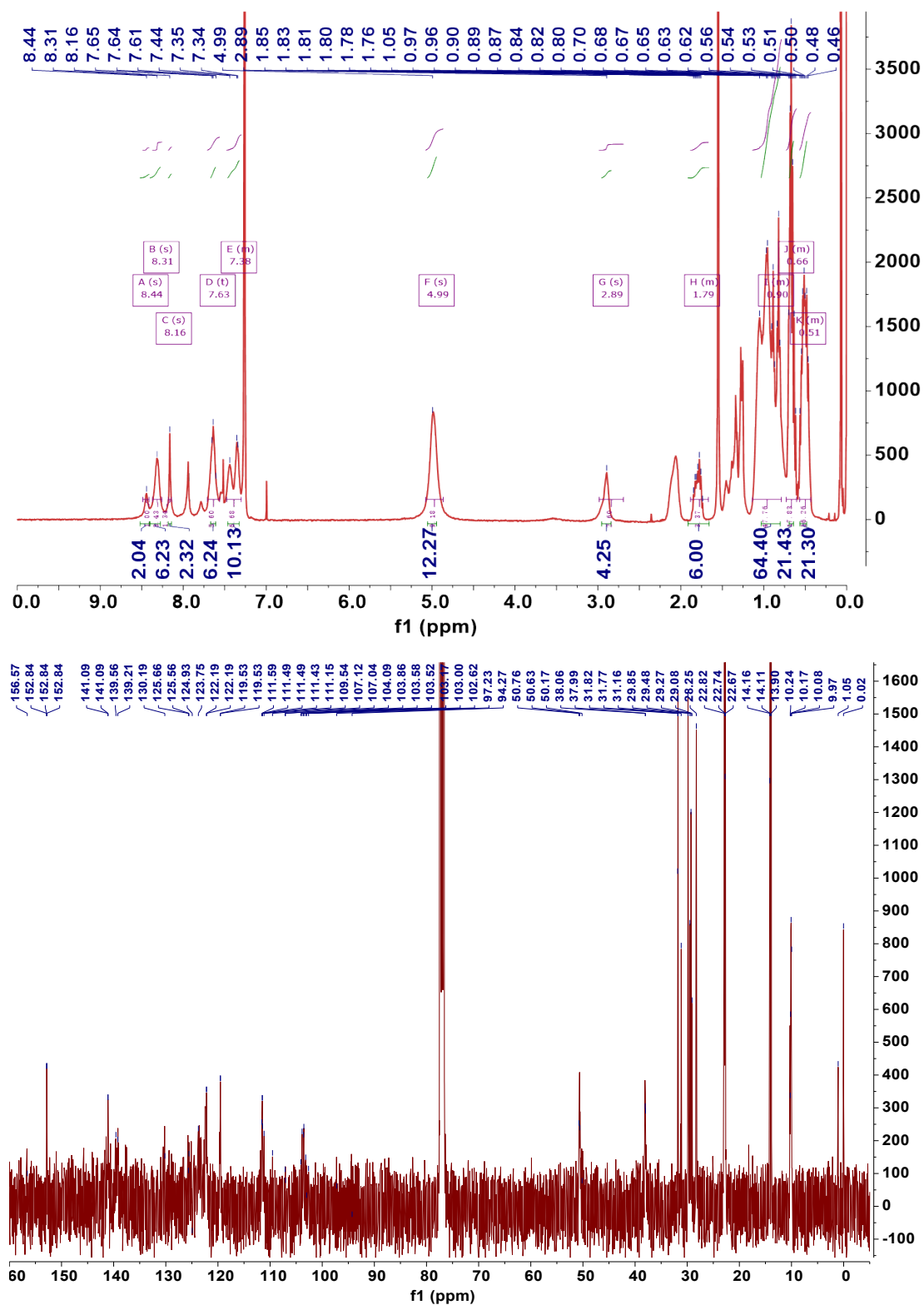


Figure S1 The ^1H NMR and ^{13}C NMR spectrum of target compound, conducted in Chloroform-d.

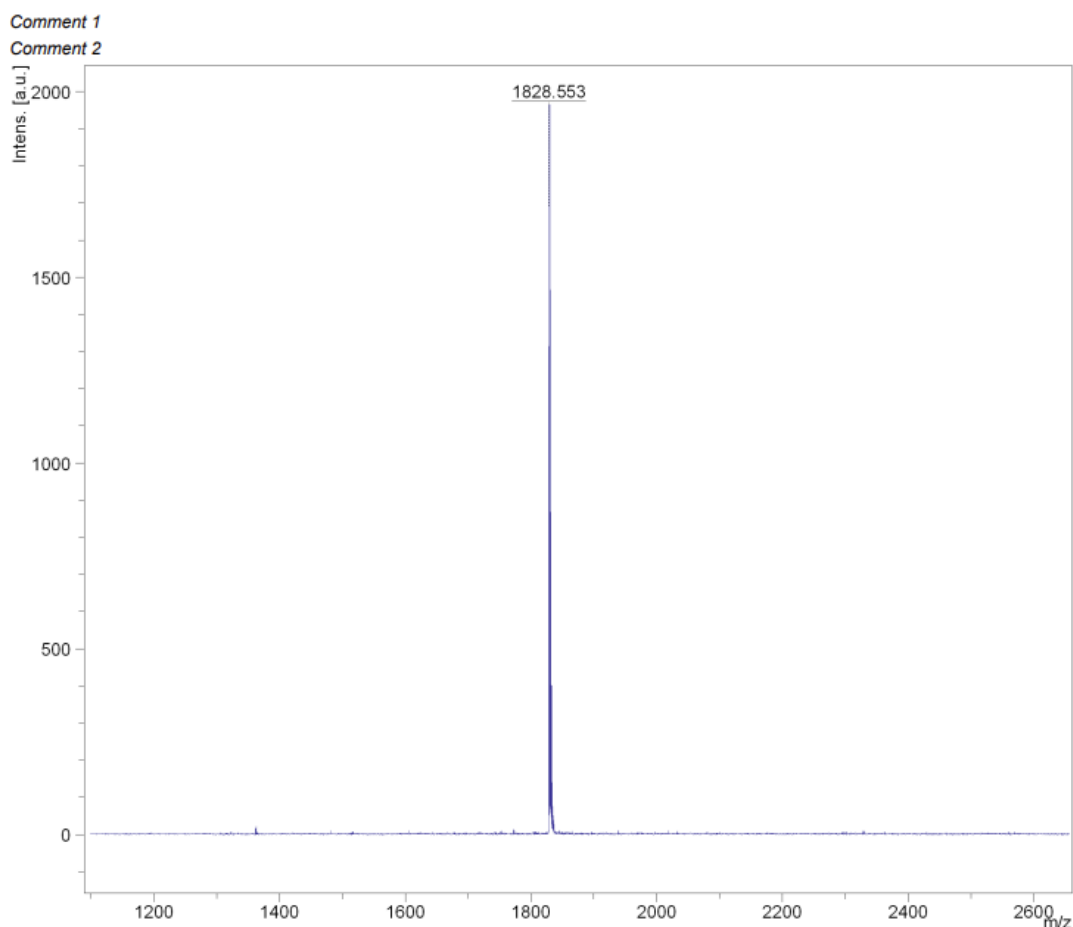


Figure S2 The MALDI-TOF MS for target compound.

2. Materials

Lead (II) oxide (Advanced Election Co., Ltd (China), 99.99%), N,N'-diphenyl thiourea (DPhTA, 98%), acetonitrile (Innochem, 99% SafeDry), Oleic acid (Sigmaaldrich, 90% technical grade), 1-Octadecene (Aladdin, >90.0% Gas chromatography), and Bis(trimethylsilyl)sulfur (TMS)₂S (TCI, 97.0% Gas chromatography), Ethyl acetate (Innochem, 99.8% water ≤ 50 ppm), Ethanol (Aladdin, 95% Analytical reagent) were employed as received for PbS QD synthesis and purification. N, N-dimethylformamide (DMF) (Innochem, 99.8% SafeDry), 1,2-Ethanedithiol (TCI 99%), Acetonitrile (Innochem 99.9% Water ≤50 ppm) were used in the ligand exchange, Isopropyl alcohol (Innochem, ≥ 99.9% Gas chromatography). All the materials were used as received unless specified.

3. Preparation of ZnO nanoparticle

A 250 mL three-neck flask was first placed on the oil bath, to which 2.95 g of zinc acetate dihydrate and 125 mL of methanol were added. The solution was then heated to

61 °C and stirred for a while. After that, 65 mL of a 0.0227 g/mL potassium hydroxide solution containing methanol as the solvent was added. This procedure took 10 to 15 min to complete. The reaction was full for 2.5 h following the addition of the potassium hydroxide solution. After 3 h of standing, discard the supernatant and mix the ZnO precipitate thoroughly with 50 mL methanol. The first wash was washed with 50 mL methanol, shook 90 s and centrifuged at 2500 rpm/2 min. The second wash was also shaken 90 s and centrifuged at 6000 rpm/3 min. Dissolve the solid with 4 mL trichloromethane and then add 16 mL methanol to form 20 mL solution.

4. Preparation of PbS-I QDs

8 mmol of PbI_2 (3.688 g) and 2 mmol of N, N-diphenylthiourea (0.4526 g) were dissolved at room temperature under stirring in 9 mL of DMF within a nitrogen-filled glovebox. After all solids were dissolved in DMF, 1 mL n-butylamine was injected into the solution, and the solution turned black immediately. After reaction for 5 min, 50 mL toluene was added as the antisolvent. After shock, centrifuge at 8000 rpm for 5 min; Then pour the waste liquid in the glove box, and then put it in the warehouse and vacuum for 12 min; The final result is a quantum dot solid of PbS-I. The PbS-I QDs solution was prepared by redispersing the QDs solid in a mixture of DMF, AC, and DMSO with a concentration of 600 mg mL⁻¹.

5. Preparation of PbS-EDT QDs

The primary technique for creating quantum dots is hot injection, which involves adding 2.25 g of PbO and 8 mL of OA to a 100 mL flask after 20 mL of ODE has been added. Before heating the solution to 85 °C, the entire flask was vacuumed for 1 h, then for 5 min, high purity nitrogen was added, and finally for 5 min of vacuuming. After the allotted time has elapsed, the temperature is increased to 122°C and the reaction is allowed to continue for an additional 40 min at 85°C. The solution should typically be transparent or have a yellowish hue if the reaction is normal. After dissolving 700 µL of $(\text{TMS})_2\text{S}$ in 5 mL of dehydrated ODE, the mixture was promptly injected into a flask containing nitrogen of the highest purity. For the synthesis of quantum dots, the main method is hot injection, which first adds 20 mL ODE to 100 mL flask, then adds 8ml OA and 2.25 g PbO. The whole flask was vacuumed for 1 h, followed by high purity nitrogen for 5 min, and then vacuumed for another 5 min before heating the solution to 85 °C. Reaction at 85 °C for 40 min, after the time is up, the temperature is raised to 122 °C, and the reaction continues for 40 min. Normally, if the reaction is normal, the solution should be transparent or yellowish in color. 700 µL of $(\text{TMS})_2\text{S}$ was then

dissolved in 5 mL of dehydrated ODE, and the solution was quickly injected into a flask with high purity nitrogen. The solution changed from transparent to black, and the reaction lasted for 1 min. After the reaction time expires, the flask is quickly lifted and 20 mL of n-hexane is injected for quenching reaction. The reaction solution is poured into the centrifuge tube and left for one night at 1~3 °C. The next day, the unreacted PbO and other impurities were removed by centrifugation at 6000 rpm/5 min. The quantum dots were washed three times with a mixture of 1:2 ethyl acetate and ethanol, and vacuum for 5 h to obtain the required high-purity quantum dots. All other operations stay the same, except for lowering the injection temperature to 100 °C to produce the smaller quantum dots required for the EDT layer.

6. PbS-QDSCs Device Fabrication

The etched ITO-coated glass was ultrasonically cleaned in a weak detergent solution for 30 minutes using ultrasound. It was then rinsed three times in deionized water. After, it was ultrasonically cleaned for 15 min using acetone, isopropanol, deionized water, sequentially, and dried. The cleaned ITO-coated glass substrates were treated by oxygen plasma activation 5 min. The ZnO layer was prepared by spin-coating a solution of nanoparticles onto the ITO substrate at 5000 rpm for 10 s. The PbS-I QDs solution was spin-coated at 2000 rpm for 40 s, followed by a 10 min annealing process within the glovebox. Subsequently, the HTMs were spin-coated (control devices: PbS solution has a 20 mg/mL concentration, while EDT solution has a 0.02% concentration. Two layers of PbS-EDT were spin-coated in the air at 3000 rpm for 10 s, after treatment with EDT solution and standing for 30s, spin coating 10 s at 3000 rpm to clean the treated film three times (ethyl acetate: acetonitrile =1:2, V : V). 3Ka-DBT-3Ka devices: small organic molecules were dissolved in chlorobenzene to create a solution with a concentration of 3 mg/ml, which was spin-coated at 3000 rpm for 10 s.) Finally, the 80 nm Au electrode was thermally evaporated on the small organic molecules film under a vacuum of 7.5×10^{-5} Pa.

7. PbS-QDSCs Characterization

The $J-V$ curves were measured by Keithley 2400 source meter. Illumination was provided by an Oriel Sol3A solar simulator (SS-F53A, Enli Technology Co. Ltd, Taiwany) with AM 1.5G spectrum and light intensity of 100 mW/cm², which was determined by a calibrated crystalline Si-cell. Simultaneously, a mask is added to the test. Each mask has eight holes with an area of 0.048 cm², which is used to evaluate the solar cell's current density more precisely. The devices were measured in reverse scan

from 0.7 V to -0.7 V with 0.02 V intervals and 10 ms delay time. By applying various filters with known optical densities to the solar cell being tested, the intensity-dependent $J-V$ curve may be derived (ThorLabs Absorbing ND Filter Kit). The QE system (EnliTech) is used to measure EQE in ambient air. Monochromatic light is focused on device pixels at a chopper frequency of 20 Hz.

8. Absorbance and Luminescence

The absorption spectra were measured by PerkinElmer Lambda650. Edinburgh FLS920 was used to test the PL of thin films and the PL of solar cells. Xe lamp was used as the excitation source to excite the thin films, and NIR-PMT (300-1700 nm) was used as the detection unit to collect PL signals.

9. Thermogravimetry Analysis (TGA) and differential scanning calorimeter (DSC)

TGA and DSC was carried out on a TA Instrument Q50 TGA under argon flow at a heating rate of 20 °C min⁻¹. The temperature of thermal degradation (Td) was measured at the point of 5% weight loss.

10. UPS spectroscopy

UPS measurements were performed using a He gas discharge lamp emitting He I radiation ($h\nu = 21.22$ eV) with a pass energy of 10 eV and a bias of -9 V to ensure secondary electron onset detection. Cluster etching was performed using large Ar clusters generated by the GCIS Ion Source (Kratos Analytical Inc.) with an energy of 10 keV.

11. AFM Measurements

The AFM images were obtained by photographing the film surface with Bruker's Dimension Icon model AFM.

12. SEM Measurements

The cross-section image of the device was investigated using a Hitach S-4800 SEM.

13. EIS Testing

Ac impedance spectroscopy was measured using an impedance analyzer (Metrohm AUTOLAB PGSTAT302N) under open circuit conditions. Frequency ranges from 0.1 kHz to 1 MHz Using EC-lab software to fit the data, the equivalent circuit diagram is determined.

14. TPV Testing

TPV measurements were performed on the Paios, Fluxim AG. TPV curves were measured at 100% offset Intensity, with a pulse length of 15 s, and a follow-up time of 5 s.

15. V_{oc} versus light intensity curves calculation

the V_{oc} ought to possess a liner correlation with the logarithm of light intensity according to Equation (2).

$$(d V_{oc})/d \lg I = 2.303 (nk_B T)/q \quad (2)$$

where k_B is the Boltzmann constant, n is the ideality factor, T is the thermodynamic temperature, and q is the elementary charge.

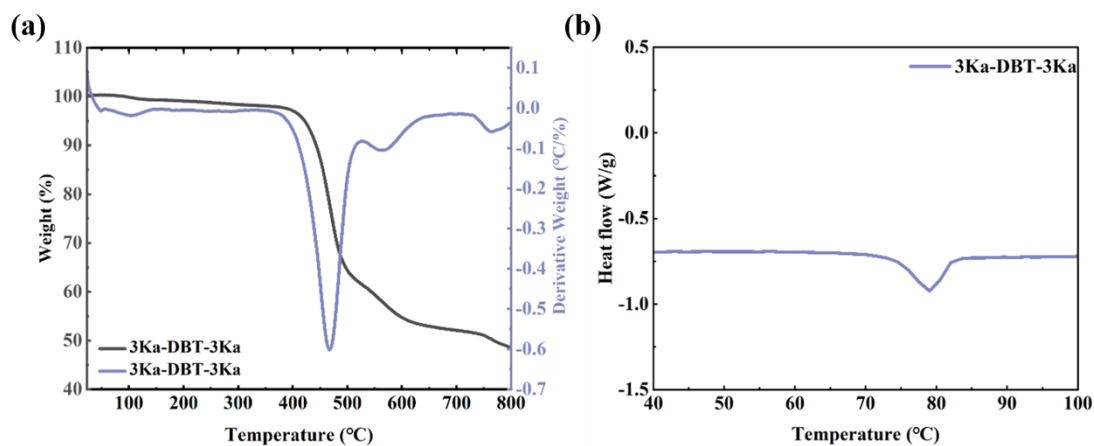


Figure S3. The spectra for 3Ka-DBT-3Ka of TGA (a) and DSC (b).

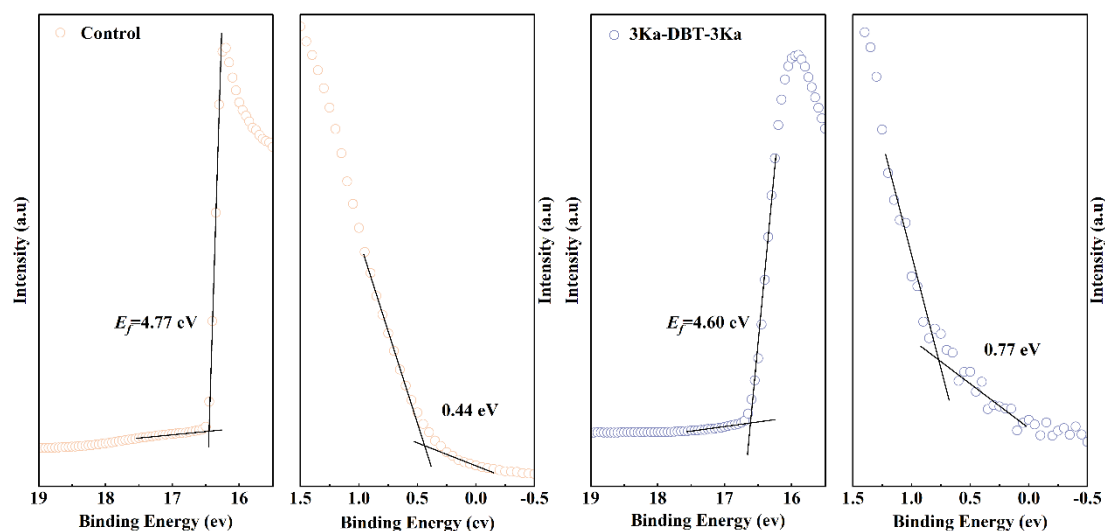


Figure S4. UPS spectra for control (EDT) and 3Ka-DBT-3Ka films, respectively.

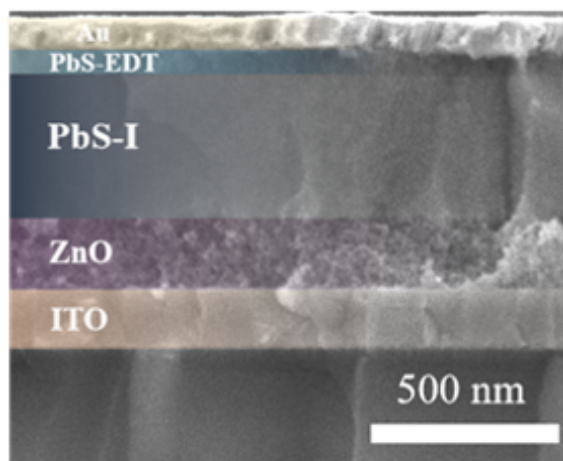


Figure S5. Cross-sectional SEM image of the control devices.

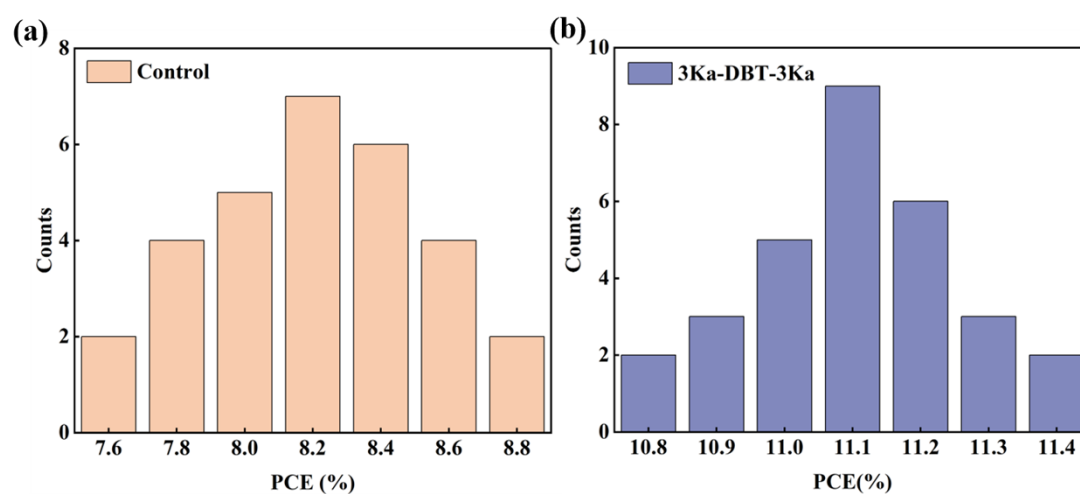


Figure S6. PCE statistical diagrams based on 30 devices.

Table S1. EIS parameters of the control (EDT as HTMs) and 3Ka-DBT-3Ka devices (3Ka-DBT-3Ka as HTMs)

Devices	R_s (Ω)	R_{tr} (Ω)	C_μ (nF)
Control	0.64	27.5	5.19
3Ka-DBT-3Ka	0.65	29.6	5.48

Reference

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- [3] L. Zhang, X. Yang, W. Wang, G. G. Gurzadyan, J. Li, X. Li, J. An, Z. Yu, H. Wang, B. Cai, A. Hagfeldt, L. Sun, *ACS Energy Lett.* **2019**, *4*, 943-951.