

Supporting Information

A novel perylene diimide-based zwitterion as the cathode interlayer for high-performance perovskite solar cells

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1. Materials and Characterization

CH₃NH₃I (MAI) was synthesized by using previously reported methods in the literature.^[1] PbI₂ (99.999%) was purchased from Alfa Aesar. PTAA, PMMA, and F4-TCNQ were purchased from Xi'an Polymer Light Technology Corp. (China). [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) and 4,7-diphenyl-1,10-phenanthroline (Bphen) were purchased from Nichem Fine Technology Co. Ltd. (Taiwan). N,N-dimethylformamide (DMF, 99.5%), dimethylsulfoxide (DMSO, 99.5%), 2-butanol (99.5%), chlorobenzene (99.5%), ethyl acetate (99.5%), and ethanol (99.5%) were purchased from Sigma Aldrich. PDI was synthesized by previously reported methods in the literature.^[2] 3,4,9,10-Perylenetetracarboxylic dianhydride, 3-aminopentane, and N,N,N'-trimethyl ethylenediamine were purchased from Aladdin (China). The indium-tin-oxide (ITO) on glass was purchased from Xiangcheng Science and Technology Co. Ltd. Other commercially available reagents were purchased from TCI Chemical Co. and used without further purification unless otherwise stated. Solvents for chemical reactions were purified according to the standard procedures. All chemical reactions were carried out under an inert atmosphere.

¹H and ¹³C NMR spectra were recorded using a 400 MHz Bruker in CDCl₃ at 293 K using TMS as a reference. The accurate mass correction was measured with matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectrometer (MALDI micro MX). UV-Vis spectra were measured with the UV-Vis spectrophotometer (Model HP8453) in a 1 cm quartz cell. Cyclic voltammetry (CV) were recorded on a BSA100B/W electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Hg/Hg₂Cl₂ electrode as the reference electrode. 0.05 M tetrabutylammonium-hexafluorophosphate (Bu₄NPF₆) dissolved in dichloromethane was employed as the supporting electrolyte, which was calibrated by the ferrocene/ferrocenium (Fc/Fc⁺) as the redox couple. The energy level of Fc/Fc⁺ is 5.08 eV relative to vacuum.

Thermal gravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/SDTA 851e at a heating rate of 10 °C min⁻¹ under the nitrogen flow of 20 mL min⁻¹.

2. Device fabrication and characterization

2.1. Device fabrication

The 5 mg mL⁻¹ 5 wt% F4-TCNQ doped PTAA precursor solution was prepared by dissolving PTAA and F4-TCNQ in chlorobenzene. The 0.5 mg mL⁻¹ PMMA precursor solution was prepared by dissolving PMMA in ethyl acetate. The MAPbI₃ precursor solution was prepared by dissolving 1.037 g PbI₂ and 0.376 g MAI (PbI₂: MAI molar ratio = 1:1.05) into 1.35 mL DMF and 0.15 mL DMSO mixed solvent. The 20 mg mL⁻¹ PCBM precursor solution was prepared by dissolving PCBM in chlorobenzene. The 1 mg mL⁻¹ QAPDI precursor solutions were prepared by dissolving QAPDI in 2-butanol. The 0.7 mg mL⁻¹ Bphen precursor solution was prepared by dissolving Bphen in ethanol.

The perovskite solar cells were fabricated as follows. First, the indium tin oxide (ITO) substrates (2×2 cm²) were ultrasonically and subsequently cleaned with deionized water, acetone, and isopropanol for 15 min, respectively. Then, the substrates were dried by blowing nitrogen and then treated with O₃ plasma for 15 min before use. After that, a PTAA:F4-TCNQ precursor solution was spin-coated on the cleaned ITO at 6000 revolutions per minute (rpm) for 20 s. Then, the films were annealed at 100 °C on a hot plate for 2 min. For the deposition of the thin passivation layer, the PMMA precursor solution was spin-coated on the top of the ITO/PTAA:F4-TCNQ substrates at 6000 rpm for 20 s, and then annealed at 100 °C for 2 min. After the substrates were cooled down, the MAPbI₃ precursor solution was spin-coated on the ITO/PTAA:F4-TCNQ/PMMA substrate at 6000 rpm for 20 s. 2-Butanol (300 μL) was used as the anti-solvent and was dropped on the wet MAPbI₃ precursor film at the eighth second during the spin-coating process, and then the films were annealed at 100 °C for 10 s. The above spin-coating processes were conducted in a glove box under a nitrogen atmosphere and

with a real-time humidity of <1 ppm. Finally, the perovskite films were transferred on a hot plate at $100\text{ }^{\circ}\text{C}$ for 15 min. After the films were cooled down, the PCBM precursor solution was spin-coated on the perovskite film at 2500 rpm for 30 s. Then, the Bphen or QAPDI precursor solution was spin-coated at 6000 rpm for 20 s without additional annealing. The devices were completed by evaporating a 100 nm thick aluminum film as the electrode. The active device area was set as 0.12 cm^2 ($0.3\times 0.4\text{ cm}^2$) by the overlapping area between the top Al cathode and the bottom ITO anode.

The electron-only devices for PCBM or QAPDI films were fabricated as follows. The 1.5 M ZnO precursor solution was spin-coated on the cleaned ITO at 4000 rpm for 30 s and then annealed at $200\text{ }^{\circ}\text{C}$ for 30 min. After the films were cooled down, the 20 mg mL^{-1} PCBM or QAPDI chlorobenzene solution was spin-coated at 1000 rpm for 30 s without additional annealing. Finally, Ca (10 nm) and Al (100 nm) films were evaporated on top of the active layer as the electrode.

The electron-only devices for perovskite films were fabricated as follows. The 0.5 M SnO_2 precursor solution was spin-coated on the cleaned ITO at 2000 rpm for 30 s and then annealed at $150\text{ }^{\circ}\text{C}$ for 30 min. The rest of the fabrication steps is similar to the fabrication of PSCs.

2.2. Device characterization

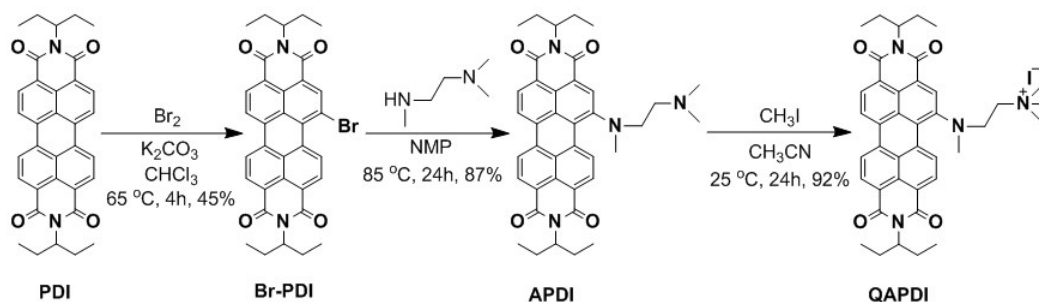
SEM images were obtained with a Zeiss Supra 55 microscope. AFM images were obtained from Bruker. A sun simulator (Zolix Sirius-SS) was used to provide the simulated solar irradiation (AM 1.5G, 100 mW cm^{-2}). J - V characteristics were measured by using a Keithley 2400 source meter. The output of the light source was adjusted using a calibrated silicon photodiode (ABET technology). The J - V curves were measured by forward scan from -0.5 to 1.5 V and reverse scan from 1.5 to -0.5 V . The EQE was measured by using a power source (Zolix Sirius-SS) with a monochromator (Zolix Omni- λ) and a source meter (Keithley 2400). The stability of the PSCs was kept in the dark condition at room temperature and under

controlled humidity of about 25%. The samples were taken out to be tested in the forward scan rate of 0.1 V/s after every 12 hours. The steady-state PL spectra were measured by the fluorescence spectrophotometer (OmniPL-microS, Zolix, China), a 600 nm continuous wave laser came into the films from the air side. Water contact angles were measured by the contact angle instrument (SZ-CAMD33, China).

References

- [1] F. Zhang, J. Song, R. Hu, Y. Xiang, J. He, Y. Hao, J. Lian, B. Zhang, P. Zeng, J. Qu, *Small*, 2018, **14**, 1704007.
- [2] H. Wang, L. Chen, Y. Xiao, *J. Mater. Chem. A*, 2017, **5**, 22288.

3. Synthesis



Scheme S1. Synthetic route of QAPDI.

Br-PDI: A mixture of PDI (1 g, 1.88 mmol) and anhydrous potassium carbonate (2.6 g, 18.85 mmol) in chloroform (20 mL) was stirred at the room temperature. Then, bromine (5.79 mL, 113 mmol) was slowly added into it under an air atmosphere, and a mixture was stirred at 70 °C after the addition of bromine was completed. After 4 hours, the excess bromine was removed by adding the saturated aqueous sodium sulfite solution. Then water was added and the mixture was extracted with chloroform. The organic layers were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the

residue was purified by silica gel column chromatography with petroleum ether:dichloromethane (1:8 v/v) as eluent to give Br-PDI (45%, 0.52 g, 0.86 mmol). ¹H NMR (400 MHz, CDCl₃, 25 °C) : δ (ppm) = 9.79-9.77 (d, 1H, Ar H), 8.92 (s, 1H, Ar H), 8.70-8.60 (m, 5H, Ar H), 5.10-5.02 (m, 2H, CH), 2.29-2.22 (m, 4H, CH₂), 1.98-1.93 (m, 4H, CH₂), 0.95-0.91 (t, 12H, CH₃).

APDI: A mixture of Br-PDI (0.50 g, 0.82 mmol) and N,N,N'-trimethyl ethylenediamine (1.07 mL 8.20 mmol) in dry 1-methyl-2-pyrrolidinone (10 mL) was stirred at 85 °C under an argon atmosphere. After 24 hours, a mixture was cooled to room temperature. Then, water was added and the mixture was extracted with chloroform. The organic layers were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography with dichloromethane:methanol (50:1 v/v) as eluent to afford APDI (87%, 0.45 g, 0.71 mmol). ¹H NMR (400 MHz, CDCl₃, 25 °C) : δ (ppm) = 9.25-9.23 (d, 1H, Ar H), 8.66-8.52 (m, 6H, Ar H), 5.10-5.07 (m, 2H, CH), 3.79-3.76 (m, 1H, CH₂), 3.73-3.33 (m, 1H, CH₂), 2.95 (s, 3H, CH₃), 2.74-2.71 (m, 1H, CH₂), 2.53-2.49 (m, 1H, CH₂), 2.29-2.24 (m, 10H, CH₂ and CH₃), 1.95-1.92 (m, 4H, CH₂), 0.95-0.91 (t, 12H, CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C) : δ (ppm) = 177.34, 175.06, 145.10, 143.64, 142.14, 140.33, 138.34, 135.18, 129.19, 127.26, 126.09, 125.48, 123.85, 122.96, 121.50, 120.33, 119.37, 113.16, 110.83, 57.53, 44.87, 41.92, 25.05, 11.36, 11.34; MALDI-TOF-MS: calculated for C₃₉H₄₂N₄O₄, 630.321 [M⁻], found 630.301.

QAPDI: A mixture of APDI (0.40 g, 0.63 mmol) and methyl iodide (59 μL 0.95 mmol) in dry acetonitrile (15 mL) was stirred at room temperature under an argon atmosphere. After 24 hours, the solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography with dichloromethane:methanol (10:1 v/v) as eluent to give QAPDI (92%, 0.45 g, 0.58 mmol). ¹H NMR (400 MHz, CDCl₃, 25 °C) : δ (ppm) = 9.46-9.44 (d, 1H, Ar H), 8.87-8.85 (d, 1H, Ar H), 8.56-8.31 (m, 5H, Ar H), 4.97-4.95 (m, 2H, CH),

4.43-4.41 (m, 2H, CH₂), 4.07-4.05 (m, 1H, CH₂), 3.74-3.66 (m, 10H, CH₂ and CH₃), 2.96 (s, 3H, CH₃), 2.24-2.20 (m, 4H, CH₂), 1.96-1.94 (m, 4H, CH₂), 0.91-0.90 (t, 12H, CH₃); ¹³C NMR (100 MHz, DMSO-d₆, 25 °C) : δ (ppm) = 171.37, 162.66, 154.35, 151.20, 144.52, 128.81, 127.30, 125.17, 122.11, 120.33, 109.65, 109.06, 100.73, 53.09, 47.50, 29.27, 24.94, 11.67; HRMS: calculated for C₄₀H₄₅N₄O₄, 645.344 [M⁺], found 645.358.

4. Supporting tables and figures

Table S1. The band structure parameters of MAPbI₃, PCBM, Bphen, and QAPDI.

Materials	Work function [eV]	Valance band maximum [eV]	E_g [eV]	<i>HOMO</i> [eV]	<i>LUMO</i> [eV]
MAPbI ₃	3.98	1.41	1.50	5.40	3.90
PCBM	4.20	2.01	2.40	6.30	3.90
Bphen	3.41	2.83	3.40	6.40	3.00
QAPDI	4.10	1.66	1.85	5.84	3.99

Table S2. Best device performance of perovskite solar cells with different QAPDI film thickness.

Thickness	J_{sc} [mA cm ⁻²]	V_{oc} [V]	<i>FF</i> [%]	<i>PCE</i> [%]
0	20.44	1.115	73.73	16.81
2	23.52	1.122	74.55	19.68
5	23.75	1.130	76.37	20.51
8	23.89	1.115	75.03	19.98
11	23.90	1.111	74.31	19.73
15	23.49	1.108	73.97	19.25

Table S3. Device performance of perylene diimide-based perovskite solar cells in the literature and this work.

Perovskite	Materials	Device Structure	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]	Ref.
MAPbI ₃	FPDI	conventional	1.08	19.8	38.5	8.25	36
MAPbI ₃	PDI-EH	inverted	0.83	19.7	61.0	10.3	37
Cs _{0.05} FA _{0.81} MA _{0.14} PbI _{2.55} Br _{0.45}	TCl-PDI	conventional	1.07	17.9	76.8	14.7	38
MAPbI ₃	di-PDI-DMBI	inverted	0.86	21.6	54.0	10.0	39
MAPbI _{2.5} Br _{0.5}	PDI	inverted	0.93	19.3	61.4	11.0	40
MAPbI ₃ (Cl)	PPDI-F3N	conventional	1.09	22.8	73.7	18.3	41
MAPbI ₃	Br-PDI	inverted	0.83	18.9	66.9	10.5	42
MAPbI _{3-x} Br _x	PPDIDTT	inverted	0.99	21.1	79.1	16.5	43
MAPbI _{3-x} Cl _x	N-PDI	conventional	1.08	21.8	75.0	17.7	44
MAPbI ₃	PDI2	conventional	1.07	23.0	78.9	19.8	45
MAPbI ₃	TPE-PDI ₄	inverted	1.05	22.0	81.0	18.8	46
MAPbI ₃	PDI-C ₆₀	inverted	1.06	22.1	79.2	18.6	47
MAPbI ₃	PV-PDI	inverted	0.93	16.6	65.6	10.1	48
Cs _{0.05} FA _{0.81} MA _{0.14} PbI _{2.55} Br _{0.45}	P(BTI-PDI)	inverted	1.12	23.3	79.1	20.6	49
FA _{0.5} MA _{0.5} PbI _{2.7} Br _{0.3}	Bis-PDI-T-EG	inverted	0.96	21.0	75.0	15.1	50
MAPbI ₃	2FBT2FPDI	inverted	1.10	23.9	77.2	20.3	51
MAPbI ₃	IDTT4PDI	inverted	1.12	23.9	74.9	20.1	52
MAPbI₃	QAPDI	inverted	1.13	23.8	76.4	20.5	This work

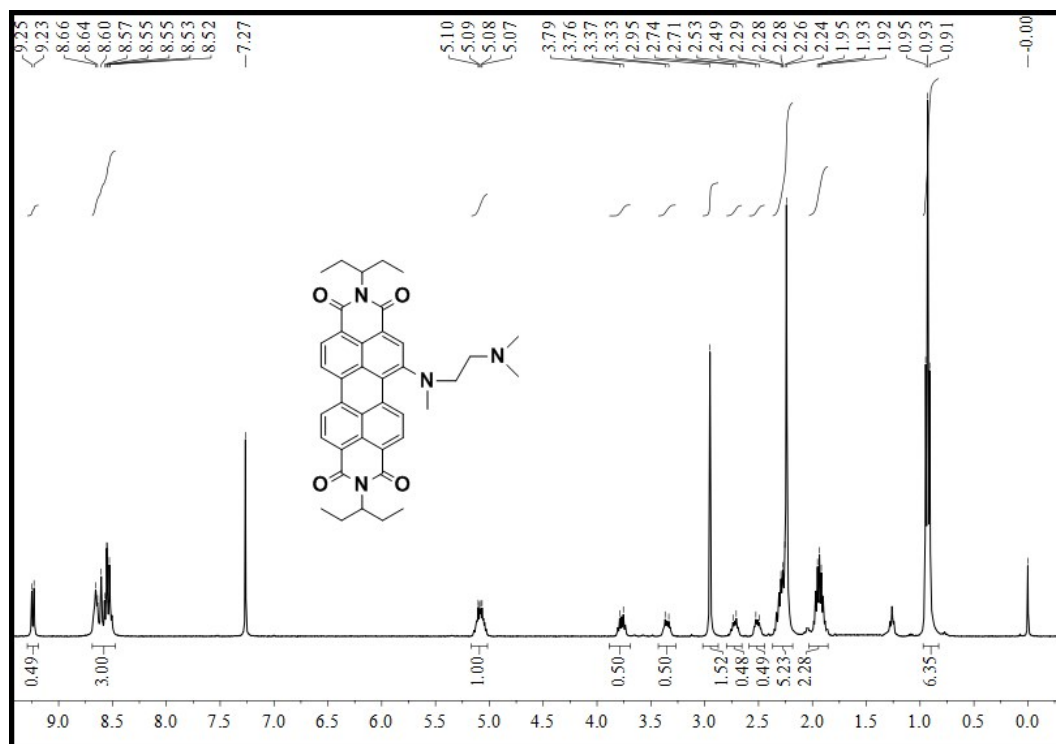


Figure S1. ¹H NMR spectrum of APDI in CDCl₃.

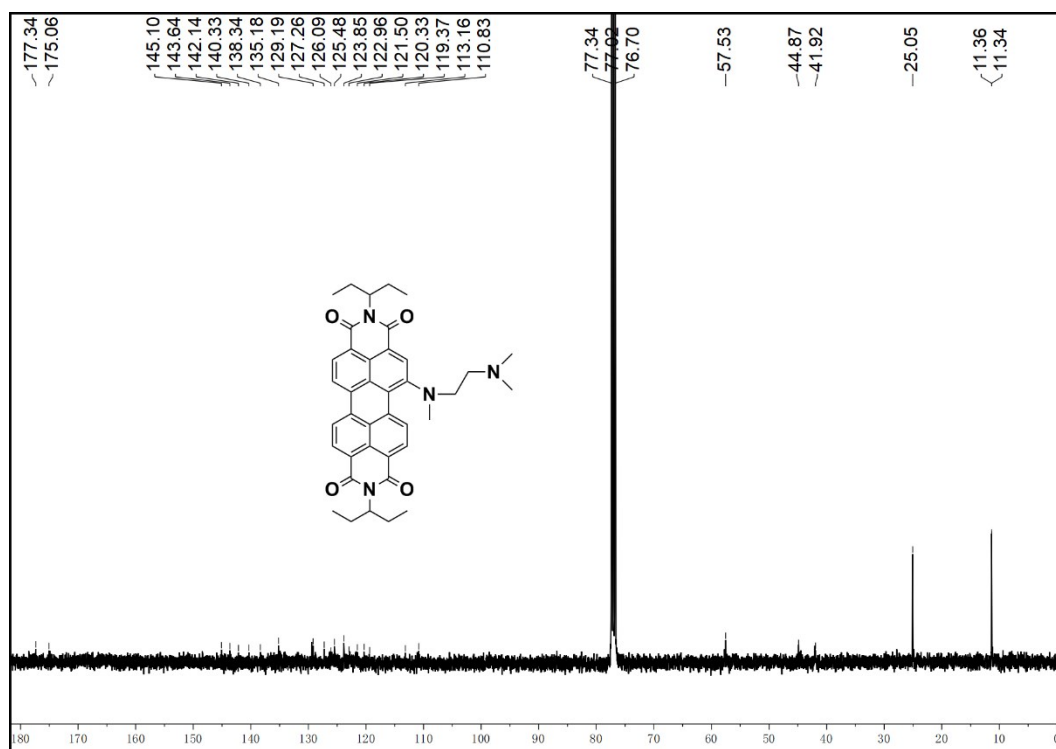


Figure S2. ¹³C NMR spectrum of APDI in CDCl₃.

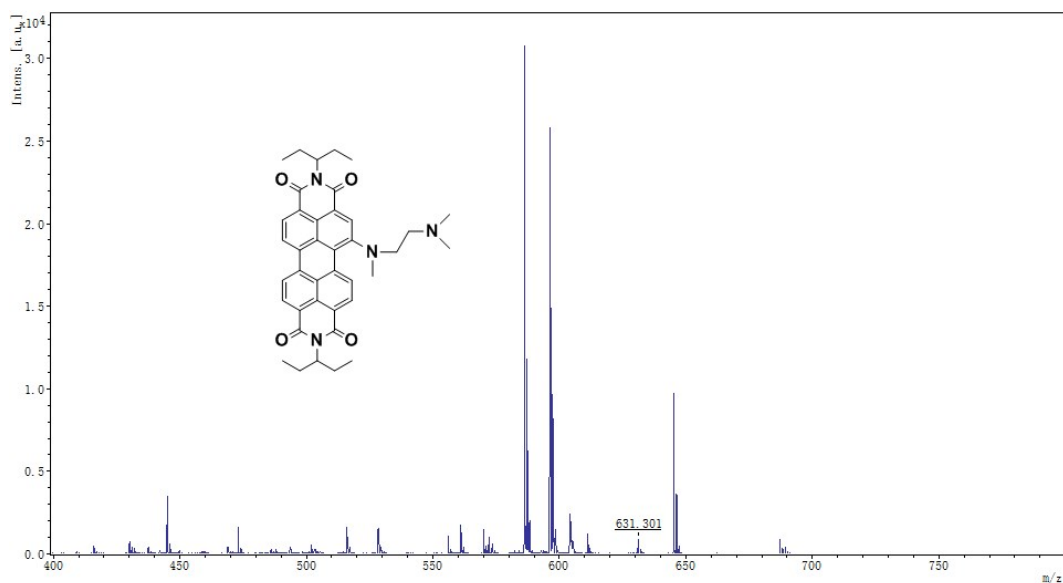


Figure S3. MALDI-TOF mass spectrum of APDI.

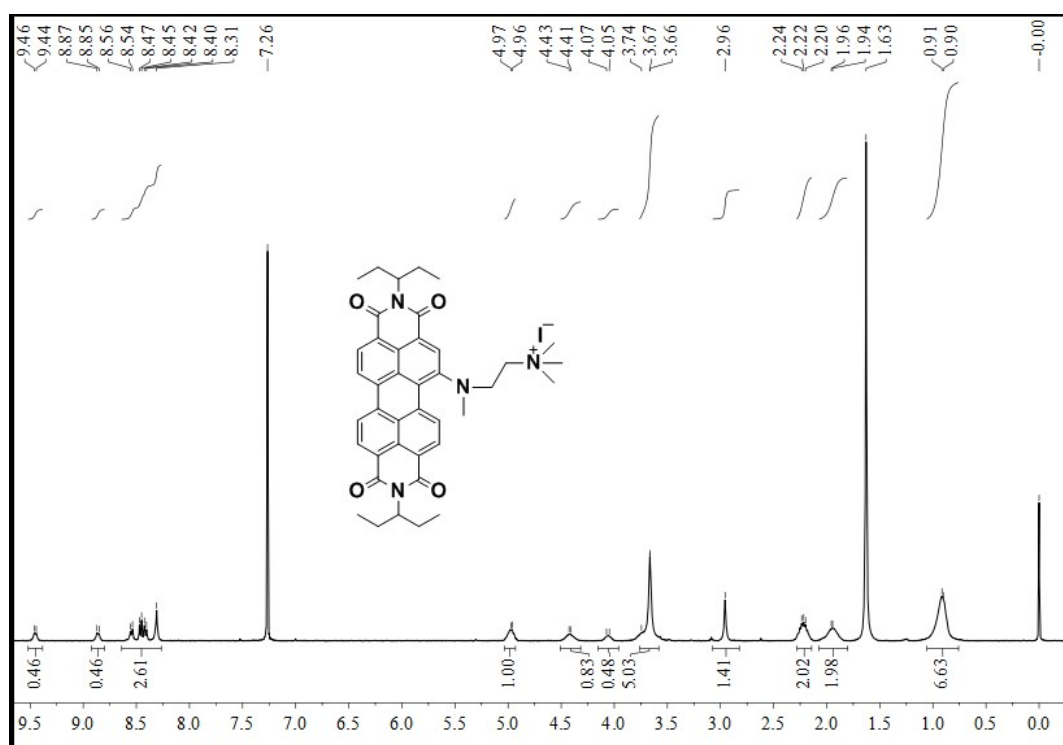


Figure S4. ¹H NMR spectrum of QAPDI in CDCl₃.

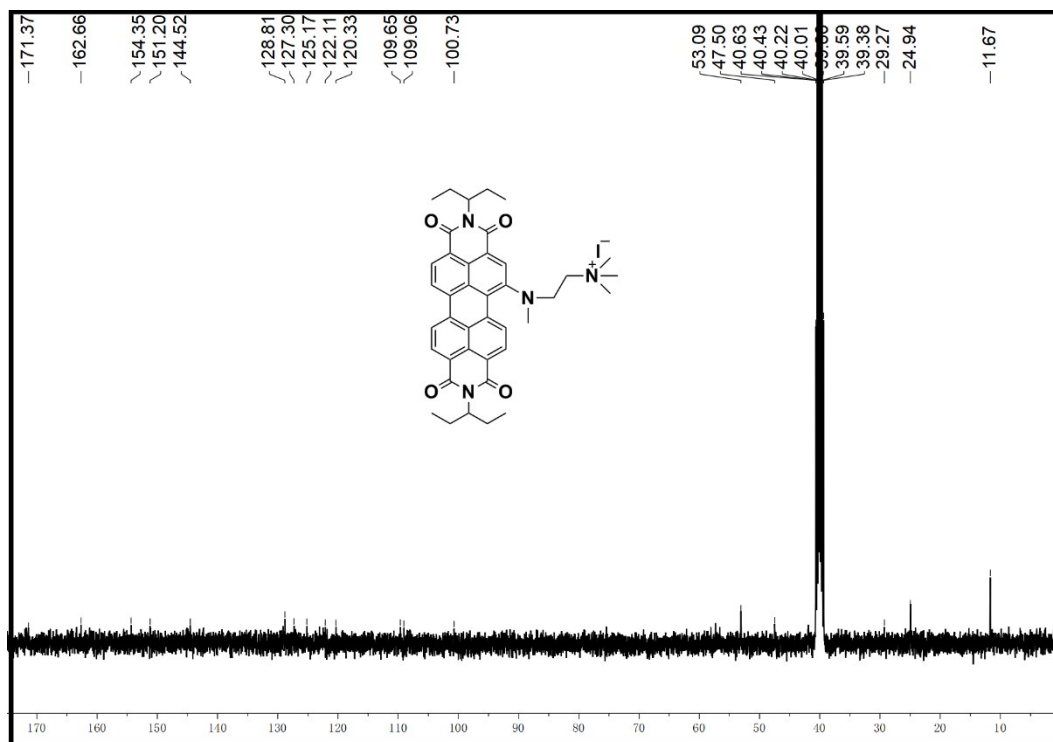


Figure S5. ^{13}C NMR spectrum of QAPDI in DMSO-d_6 .

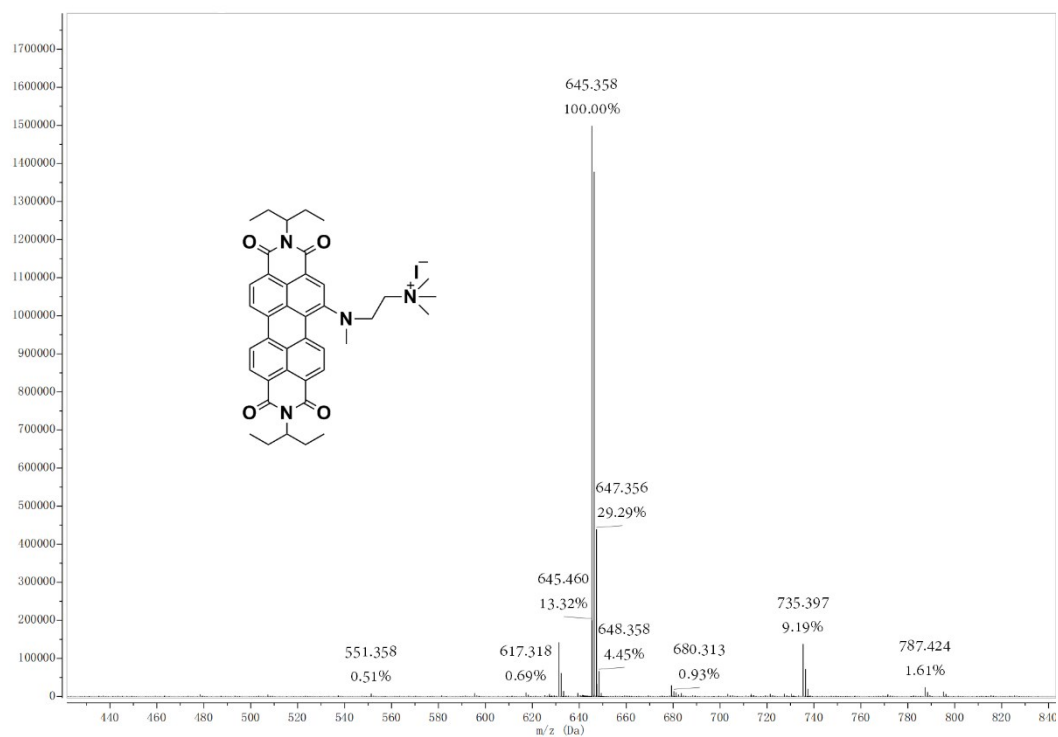


Figure S6. HRMS mass spectrum of QAPDI.

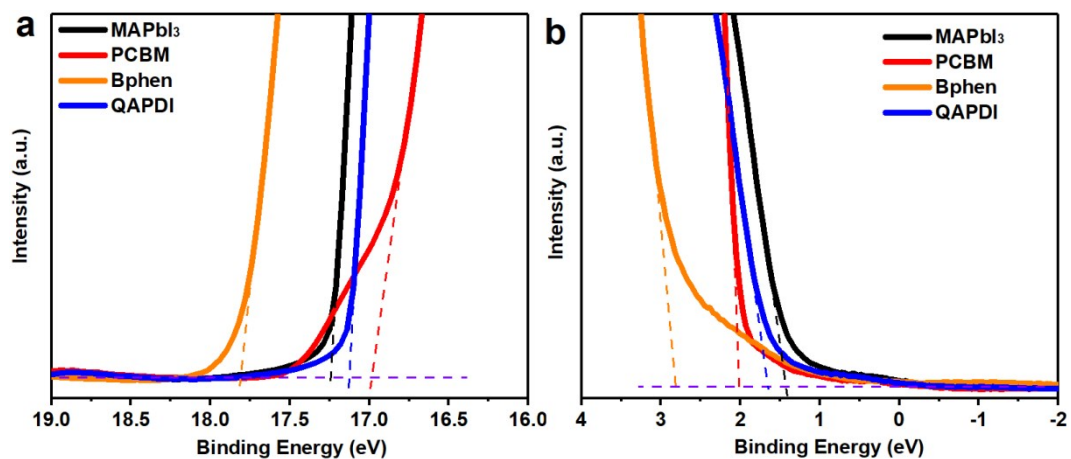


Figure S7. UPS spectra of MAPbI₃, PCBM, Bphen, and QAPDI in the high binding energy region (a) and the low binding energy region (b).

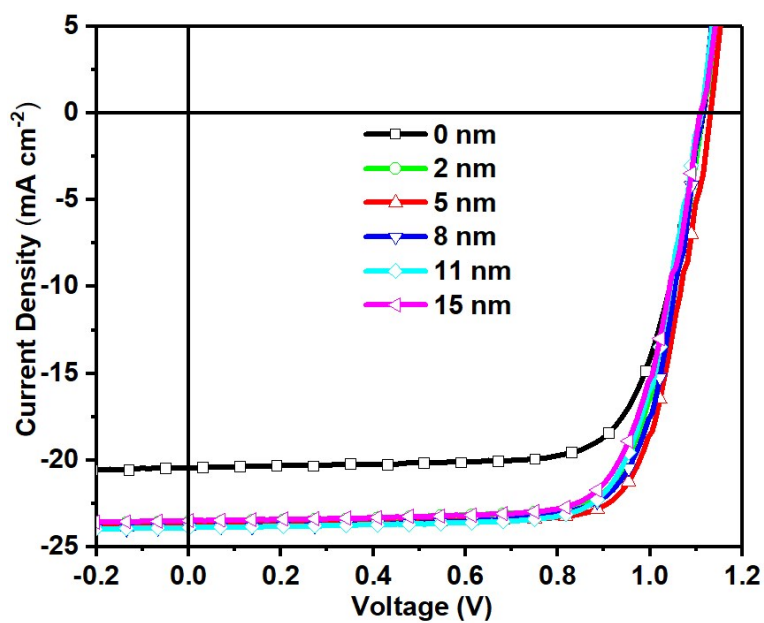


Figure S8. J - V curves of PSCs with different thickness of the QAPDI layer.

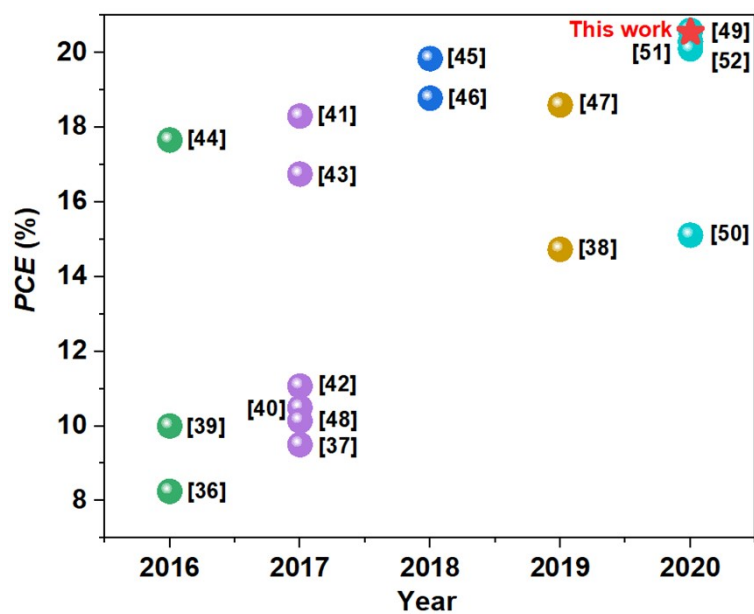


Figure S9. The device efficiency values of perylene diimide-based perovskite solar cells in the literature and this work.

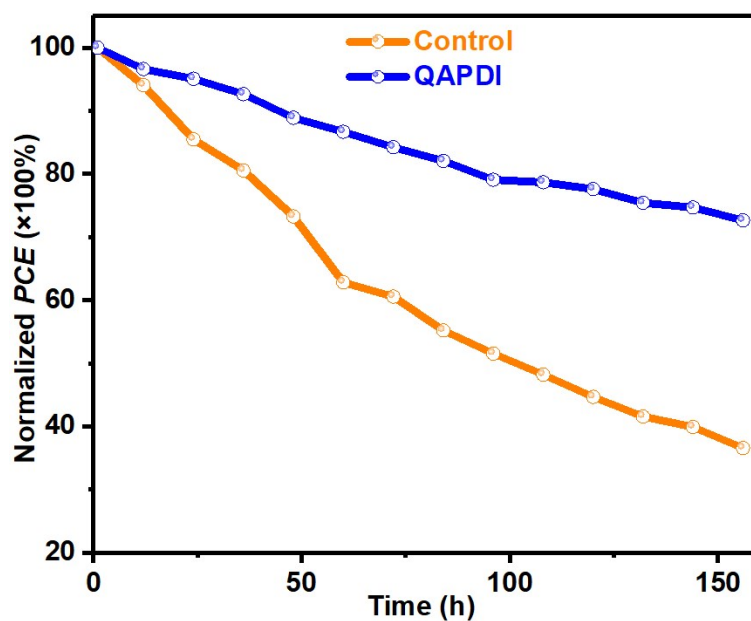


Figure S10. Stability measurement of the control and QAPDI-based devices stored in dark under 25% humidity conditions.

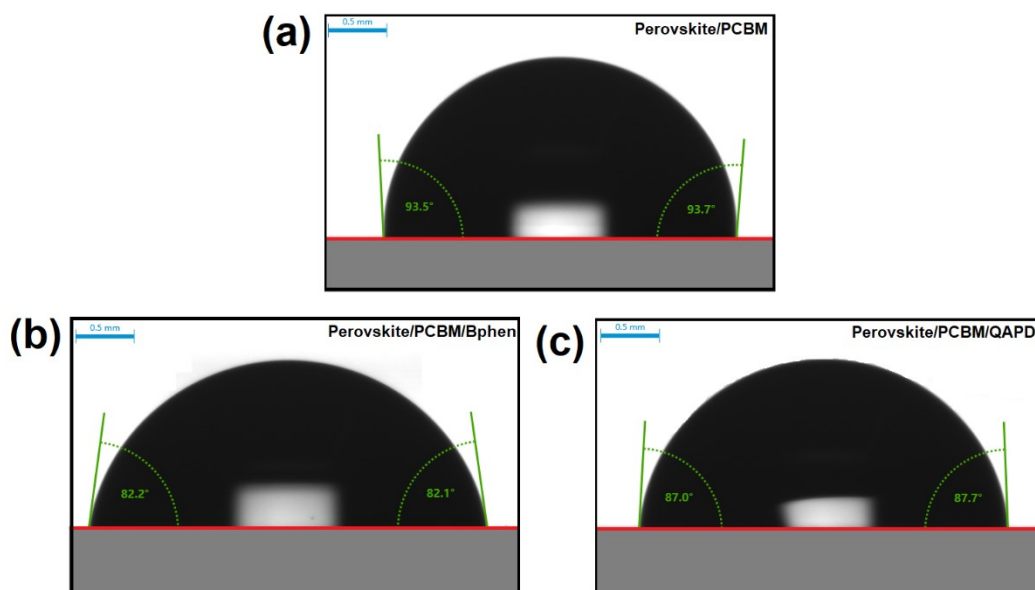


Figure S11. Water contact angles for PCBM- (a), PCBM/Bphen- (b), or PCBM/QAPDI-covered (c) MAPbI₃ films.