Electronic supplementary information
Soluble Perinone Isomers as Electron Transport Materials for p-i-n Perovskite Solar Cells

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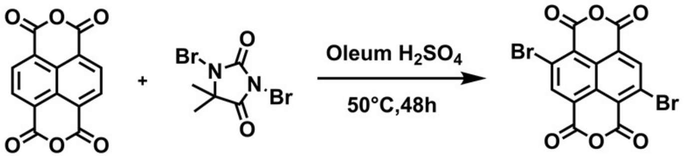
1. Materials

Unless otherwise stated, all chemicals were purchased from Aladdin., Macklin and Sinopharm Chemical Reagent Co., Ltd. 1,4,5,8-Naphthalenetetracarboxylic dianhydride and tetrakis(triphenylphosphine)palladium were purchased from Shanghai Energy Chemical Co., Ltd. Acetic acid was purchased from Shanghai Mairuier Chemical Technology Co., Ltd.

2. Synthesis

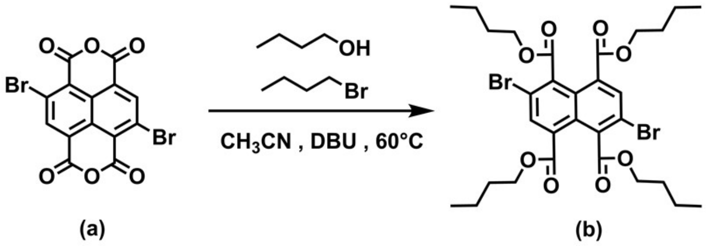
2,6-Dibromonaphthalene-1,4,5,8-tetracarboxylic Dianhydride (a)



1,4,5,8-Naphthalenetetracarboxylic dianhydride (10.00 g, 37.3 mmol) was stirred evenly in concentrated sulfuric acid (25 mL, 96%). 1,3-Dibromo-5,5-dimethylthydantoin (11.59 g, 55.9 mmol) was added into the mixture in batches within one hour. The resulting solution was stirred for 24 hours at 50 °C. After the reaction is completed, a mixture of ice and water then slowly added into the mixture. The precipitate was filtered out and rinsed with water several times until the filtrate is colorless. The crude product of compound **a** (12.72 g, 80.1% yield) was obtained by drying in vacuum and used directly for the next step.

^{1}H NMR (400 MHz, DMSO-d^6, ppm): δ = 8.76 (s, 2H).

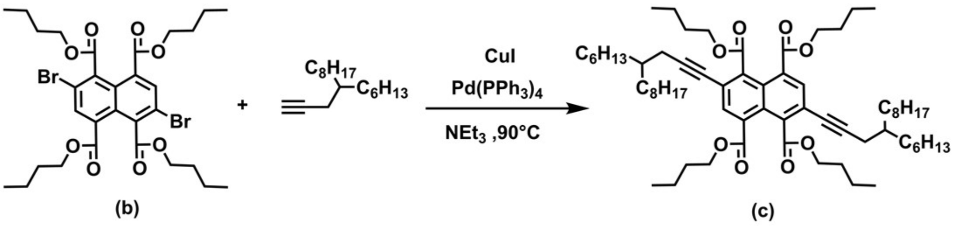
Tetrabutyl 2,6-dibromonaphthalene-1,4,5,8-tetracarboxylate (b)



Compound **a** (5.00 g, 11.7 mmol) and butyl alcohol (14.79 g, 199.6 mmol) were dissolved in the anhydrous acetonitrile (200 mL) under argon atmosphere. Then added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (16.07 g, 105.7 mmol) into the mixture. After stirring at room temperature for 30 minutes, 1-bromobutane (22.52 g, 164.4 mmol) was added to the mixture and refluxed at 80°C for 7 days. After cooling to room temperature, the solvent was removed under reduced pressure. Plenty of water was added and the precipitate was filtered and purified with column chromatography on silica gel using trichloromethane/petroleum ether (1:2, v/v) as the eluent. Finally, compound **b** (4.24 g, 52.8% yield) was obtained as a light-yellow solid.

^{1}H NMR (600 MHz, CDCl$_3$, ppm): δ = 8.05 (s, 2H), δ = 4.32-4.30 (t, *J* =6.8 Hz, 8H), δ = 1.8-1.75 (m, 8H), δ = 1.51-1.45 (m, 8H), δ = 1.00-0.96 (m, 12H).

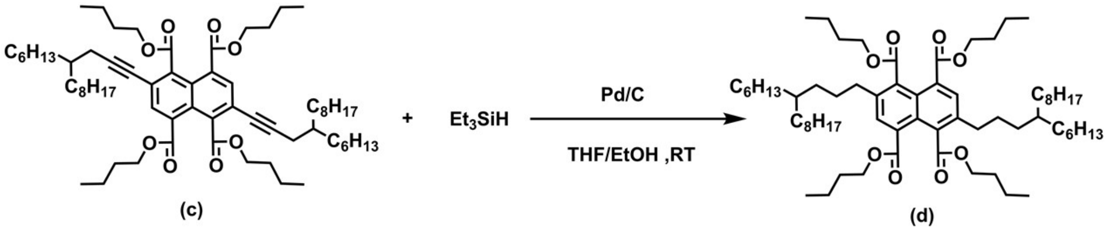
Tetrabutyl 2,6-bis(4-hexyldodec-1-yn-1-yl)naphthalene-1,4,5,8-tetracarboxylate (c)



Compound **b** (2.00 g, 2.9 mmol), CuI (13 mg, 0.07 mmol) and Pd(PPh$_3$)$_4$ (169 mg, 0.15 mmol) were mixed under argon atmosphere, and then 7-(prop-2-yn-1-yl)pentadecane (2.20 g, 8.7 mmol) and triethylamine (30 mL) were added into the system. After refluxing at 90 °C overnight, the mixture was cooled to room temperature and water was added. The mixture was extracted with petroleum ether. The organic phase was combined and dried over sodium sulfate and filtered. Under reduced pressure, the solvent was removed. The crude product was chromatographically purified on a silica gel column eluting with trichloromethane /petroleum ether (1/2, v/v) to afford compound (**c**) as a yellow oil (2.94 g, 98.1% yield).

^{1}H NMR (600MHz, CDCl$_3$) δ = 7.88 (s, 2H), δ = 4.68 (s, 2H), δ = 4.36-4.25 (m, 8H), δ = 2.44-2.43 (d, *J* = 5.9 Hz, 4H), δ = 2.00-1.97 (t, *J* = 2.0 Hz, 6H), δ = 1.76-1.73 (m, 8H), δ = 1.63-1.59 (m, 2H), δ = 1.49-1.27 (m, 48H), δ = 0.89-0.85 (m, 24H).

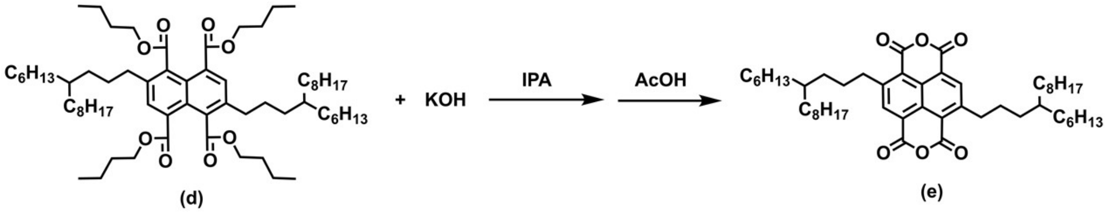
Tetrabutyl 2,6-bis(4-hexyldodecyl)naphthalene-1,4,5,8-tetracarboxylate (d)



Compound **c** (500 mg, 0.5 mmol) and Pd/C (108 mg, 0.1 mmol) were added into a double neck flask at argon atmosphere. Then THF (20 mL) and EtOH (10 mL) which deoxygenated with argon for one hour were added. After stirring for 30 minutes, added Et_3SiH (0.78 mL, 4.9 mmol) drop by drop within 3 hours. After stirring for another 20 h, water was added and the mixture was extracted with trichloromethane. The organic phase was combined and dried over Na_2SO_4. Removing the solvent under reduced pressure gave the crude product. The crude product was chromatographically purified on a silica gel column eluting with trichloromethane/petroleum ether (1/3, v/v) and recrystallized with MeOH to obtain the compound **d** (305 mg, 61.4% yield) as a white solid.

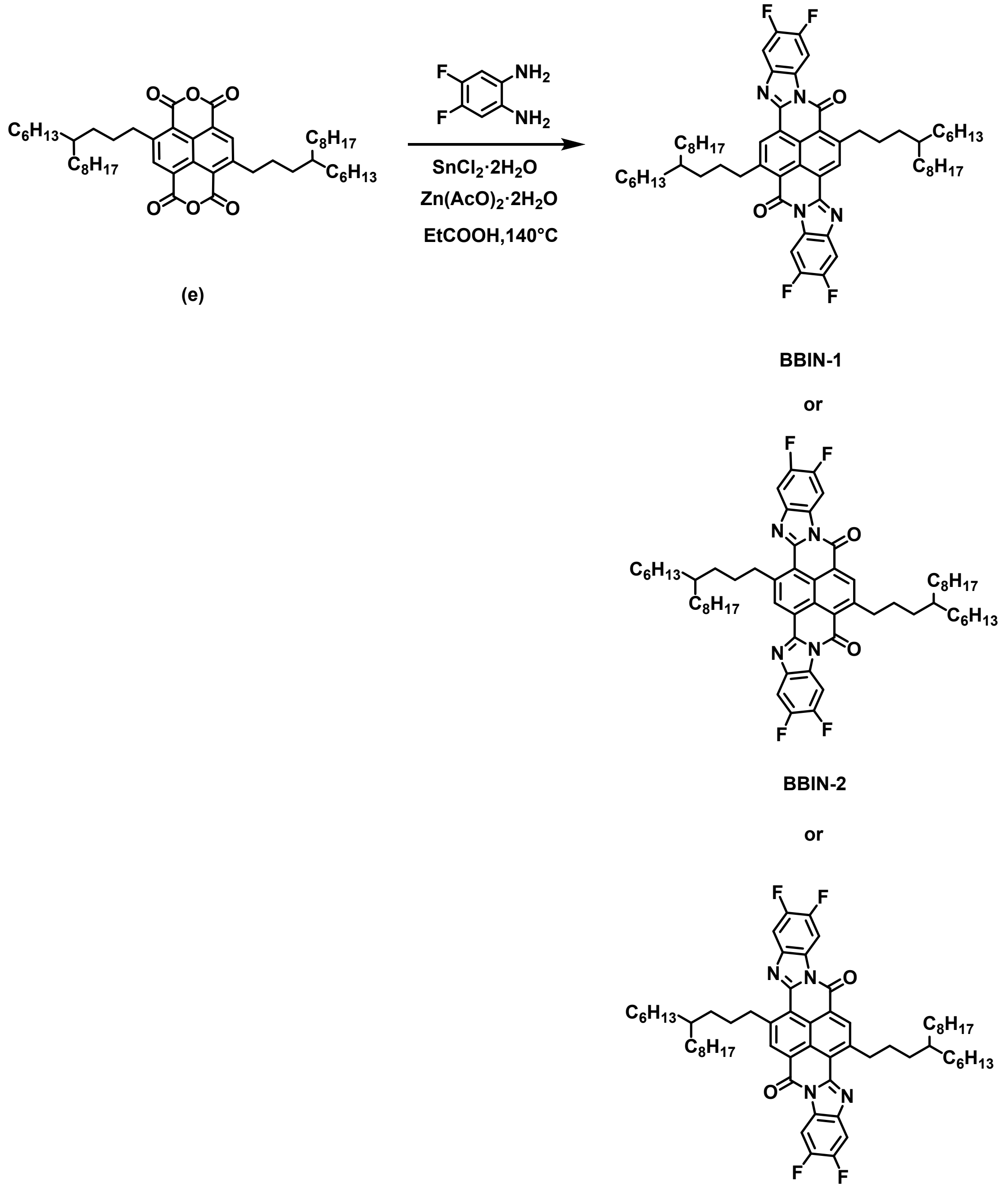
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.74 (s, 2H), δ = 4.31-4.29 (t, J = 6.8 Hz, 4H), δ = 4.27-4.24 (t, J = 6.9 Hz, 4H), δ = 2.85-2.82 (t, J = 7.9 Hz, 4H), δ = 1.78-1.69 (m, 8H), δ = 1.64-1.58 (m, 8H), δ = 1.49-1.39 (m, 8H), δ = 1.29-1.22 (m, 50H), δ = 0.99-0.94 (m, 12H), δ = 0.89-0.86 (t, J = 6.9 Hz, 12H).

4,9-Bis(4-hexyldodecyl)isochromeno[6,5,4-def]isochromene-1,3,6,8-tetraone (e)



Compound **d** (750 mg, 0.7 mmol) and KOH (4135.3mg, 74 mmol) were dissolved in 50 mL of IPA and refluxed at 90 °C overnight. The reaction mixture concentrated under reduced pressure until most of the solvent was removed. After adding water (150 mL), a white solid is obviously produced. Then HCl was added to make the solution acidic. After stirring for one hour, the precipitate was filtrated and dried. Then added the solid to AcOH (60 mL) and refluxed at 120°C overnight. After cooling to room temperature, water was added and the mixture was extracted with $CHCl_3$. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After removing organic solvents, the crude product of compound **e** was obtained by silica gel column chromatography with $CHCl_3$/petroleum ether (1/1, v/v) as eluent. Without further purification, the compound **e** (413 mg, 72.5% yield) was used directly in the following reaction.

BBIN



(e)

BBIN-1

or

BBIN-2

or

BBIN-3

Compound **e** (410 mg, 0.5 mmol), 4,5-difluorobenzene-1,2-diamine (229 mg, 1.6 mmol), $SnCl_2$•$2H_2O$ (12 mg, 0.05 mmol) and $Zn(AcO)_2$•$2H_2O$ (12 mg, 0.05 mmol) were dissolved in 20 mL of EtCOOH under argon atmosphere. After refluxing for 24 h, water (100 mL) was added, and solids appeared. After stirring for 1 h, the precipitate was filtered and chromatographically purified on a silica gel column eluting with PE/CF (2:1, v/v) to afford the **BBIN** (369 mg, 70.6% yield), including **BBIN-1** (126 mg, 34%), **BBIN-2** (107 mg, 29%) and **BBIN-3** (136 mg, 37%).

^1H NMR (**BBIN-1**) (600 MHz, $CDCl_3$ and TFA-d) $\delta = 9.19$ (s, 2H), $\delta = 8.66$-8.64 (t, $J = 7.1$ Hz, 2H), $\delta = 7.89$ (s, 2H), $\delta = 3.81$ (br, 4H), $\delta = 2.08$ (s, 4H), $\delta = 1.33$ (s, 26H), $\delta = 0.90$-0.88 (m, 16H), $\delta = 0.48$ (s, 16H), $\delta = 0.44$ (s, 4H), $\delta = 0.28$-0.26 (t, $J = 6.0$ Hz, 2H), δ = 0.20 (s, 2H). TOF-MS: Exact Mass for $C_{62}H_{81}F_4N_4O_2$ [M+H]$^+$: 989.6217; found: 989.6334.

^{1}H NMR (**BBIN-2**) (600 MHz, $CDCl_3$ and TFA-d) δ = 9.10-9.09 (d, *J* = 4.2 Hz, 2H), δ = 8.76-8.73 (m, 1H), δ = 8.50-8.47 (m, 1H), δ = 7.95-7.92 (m, 1H), δ = 7.83-7.80 (m, 1H), δ = 3.82-3.74 (m, 4H), δ =1.91 (s, 4H), δ = 1.66-1.61 (m, 4H), δ = 1.51-1.43 (m, 2H), δ = 1.36-1.25 (m, 48H), δ = 0.90-0.84 (m, 12H). TOF-MS: Exact Mass for $C_{62}H_{81}F_4N_4O_2$ [M+H]$^+$: 989.6217; found: 989.6347.

^{1}H NRM (**BBIN-3**) (600 MHz, $CDCl_3$ and TFA-d) δ = 9.20 (s, 2H), δ = 8.76-8.74 (t, *J* = 7.4Hz, 2H), δ = 7.98-7.96 (t, *J* = 7.0 Hz, 2H), δ = 3.74-3.71 (t, *J* = 7.7 Hz, 4H), δ = 1.90-1.85 (m, 4H), δ = 1.68-1.64 (m, 4H), δ = 1.35 (s, 12H), δ = 1.31-1.28 (s, 42H), δ = 0.87-0.85 (m, 20H). TOF-MS: Exact Mass for $C_{62}H_{81}F_4N_4O_2$ [M+H]$^+$: 989.6217; found: 989.6342.

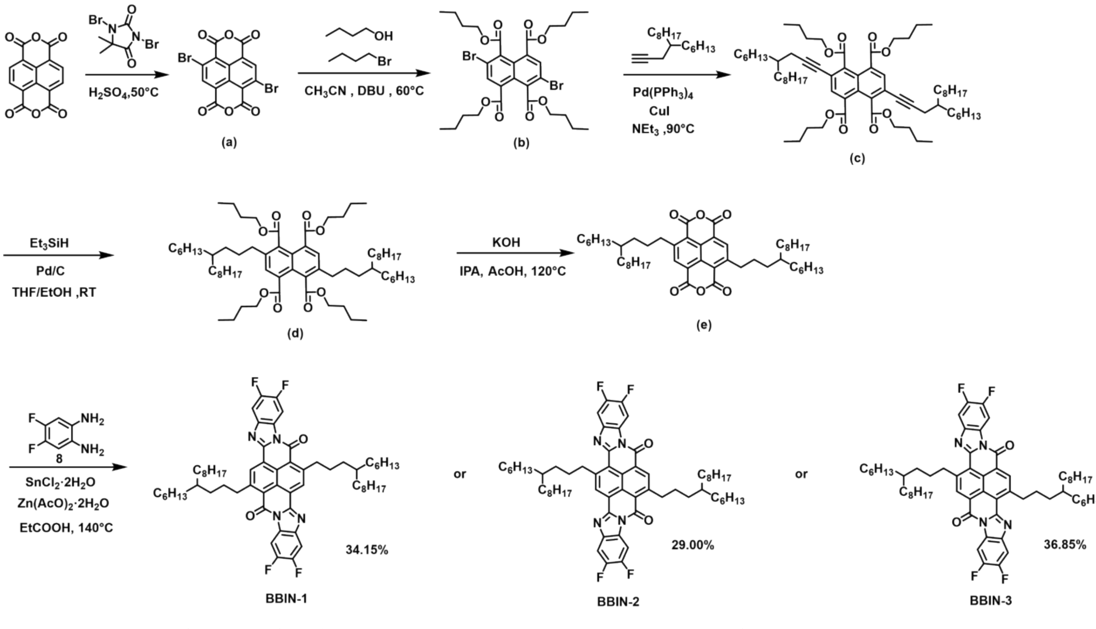
3. **Device fabrication**

Firstly, the ITO substrates (Rs ≤ 15 Ω sq^{-1}, transmittance ≥ 86%, 2 cm x 2 cm) were successively ultrasonic cleaned with detergent, deionized water, acetone and isopropanol for 15 min. Then the ITO substrates were dried under nitrogen flow and treated in O_2-plasma for 5 minutes. After that, 40 μL of P3CT (Rieke, America) solution (1 mg mL^{-1}in methanol) was taken and spin-coated on the clean ITO at 4000 rpm for 30 s, followed by thermally annealing at 100 °C for 10 min in air. The perovskite precursor solution (1.20 M) was prepared by dissolving FAI:PbI_2 (1:1 molar ratio) in 1 mL *N,N*-dimethylformamide/dimethyl sulfoxide (4/1, v/v) solvent, and was deposited on P3CT by spin-coating sequentially at 2000 and 4000 rpm for 10 and 20 s, respectively. Here, at about 20 s after starting the spin-coating, 150 μL of chlorobenzene was dropped on the substrate. Then the perovskite layer was annealed at 145 °C for 10 minutes to assist in the formation of the perovskite crystalline grain. Furthermore, different ETMs were deposited on ITO/P3CT/perovskite by spin-coating at 2000 rpm for 30 s. Finally, C_{60} (20 nm), BCP (8 nm) and Ag (100nm) were successively deposited by vacuum evaporation. The area of all components is 9 mm^2.

4. Measurements and characterization

^{1}H NMR spectrum was measured on the Bruker Advance III 600 MHz NMR spectrometer, using tetramethylsilane (TMS) as the internal standard at room temperature. Mass spectrometry (MS) was studied by time-of-flight mass spectrometer on a 4600 LC-Q-TOF with CH_2Cl_2 as the solvent. Thermogravimetric analysis (TGA) was recorded on a TA Q5000IR tr at a heating rate of 10.0 K/min in nitrogen atmosphere. Cyclic voltammetry (CV) measurements were made in a solution of tetra-n-butylammonium-hexa-fluorophosphate (0.1 M) in a nitrogen atmosphere using a CS310M electrochemical workstation. Using a conventional three-electrode cell with a platinum disk electrode working electrode, a Pt wire gauze as the counter electrode, and a Ag/AgCl as the reference electrode, respectively. The film was prepared by dropping BBIN solution on the working electrode. Ferrocene/ferrocenium

(Fc/Fc$^+$) was used as the internal standard (the energy level of Fc/Fc$^+$ in vacuum is -4.8 eV).The calculation of LUMO energy level uses formula $\mathrm{LUMO} = -\left(4.8 + E_{\mathrm{onset}}^{\mathrm{red}} - E_{\mathrm{onset}}^{\mathrm{Fc}}\right)\,\mathrm{eV}$, in which $E_{\mathrm{onset}}^{\mathrm{red}}$ is the initial reduction potential $E_{\mathrm{onset}}^{\mathrm{Fc}}$ is equal to the initial oxidation potential of ferrocene, and HOMO = LUMO - Eg. UV-Vis spectra were recorded from 320 to 700 nm on a GS54T spectrophotometer (Shanghai Refrigeration Technology Co., Ltd.). The electron mobility (μ_e) was calculated with the Mott-Gurney square law by the equation $J = \frac{9\varepsilon_0\varepsilon_r\mu}{8L^3}V^3$, where J stands for the current density, ε_0 is the free-space permittivity, ε_r is the dielectric constant of the ETM, V is the effective voltage, L is the thickness of the ETM film and μ is the charge mobility. The surface of the device was observed by scanning electron microscope (SEM) (S4800, Hitachi, Japan). The surface roughness was tested by AFM (Dimension 3100, Vico, USA). The steady-state photoluminescence (PL) spectroscopy is carried out by a fluorescence spectrophotometer (F-4600, Hitachi Co., Ltd., Tokyo, Japan). The current density-voltage (*J-V*) characteristics were measured with a Keithley 2440 source meter at -0.2 to 1.2 V in a glove box under simulated AM 1.5G (100 mW cm^{-2}) irradiation. EQE was conducted by a Newport EQE system (Enlitech, QE-R3011) in the atmosphere.



Scheme S1. The synthesis routes of BBIN-1; BBIN-2 and BBIN-3.

Table. S1 Solubility of the BBIN series in different solvents at room temperature.

Solvents **ETMs**	**CF**	**CB**	**DCB**	**IPA**
BBIN-1	3 mg/mL	4 mg/mL	3 mg/mL	0.5 mg/mL
BBIN-2	4 mg/mL	4 mg/mL	4 mg/mL	0.5 mg/mL

BBIN-3	3 mg/mL	4 mg/mL	4 mg/mL	0.5 mg/mL

Table S2 Photovoltaic performance of PSCs modified by BBIN series with different concentrations.

ETM	C (mg/mL)	*Voc* (V)	*Jsc* (mA/cm^2)	*FF* (%)	*PCE* (%)
BBIN-1	0.5	1.057	24.23	71.80	18.38
	1	1.061	23.52	75.00	18.71
	2	1.048	23.68	73.00	18.11
	3	1.037	23.67	70.30	17.28
BBIN-2	0.5	1.00	23.89	75.92	18.18
	1	1.06	23.59	77.10	19.36
	2	1.01	24.18	76.96	18.74
	3	1.04	23.43	73.31	17.93
BBIN-3	0.5	1.024	23.79	70.77	17.24
	1	1.044	24.05	70.73	17.77
	2	0.964	23.54	75.56	17.15
	3	0.971	23.05	73.34	16.43

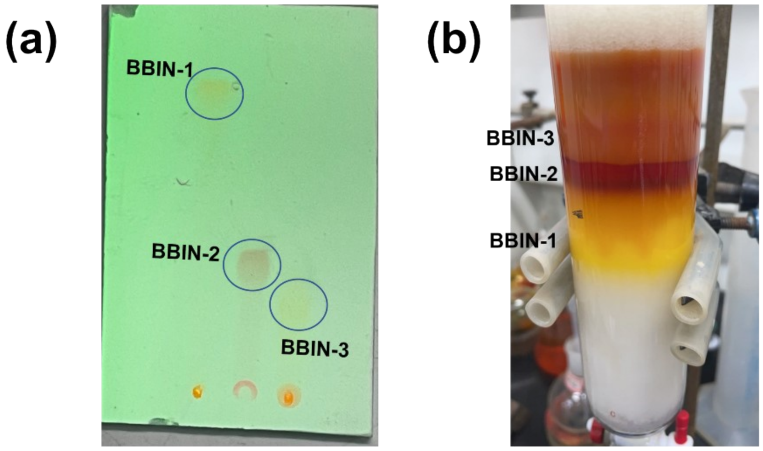


Fig. S1 Pictures of BBIN-1, BBIN-2 and BBIN-3 in (a) silica gel plate (b), silica gel column, with petroleum ether/chloroform (v/v, 2:1) as eluant.

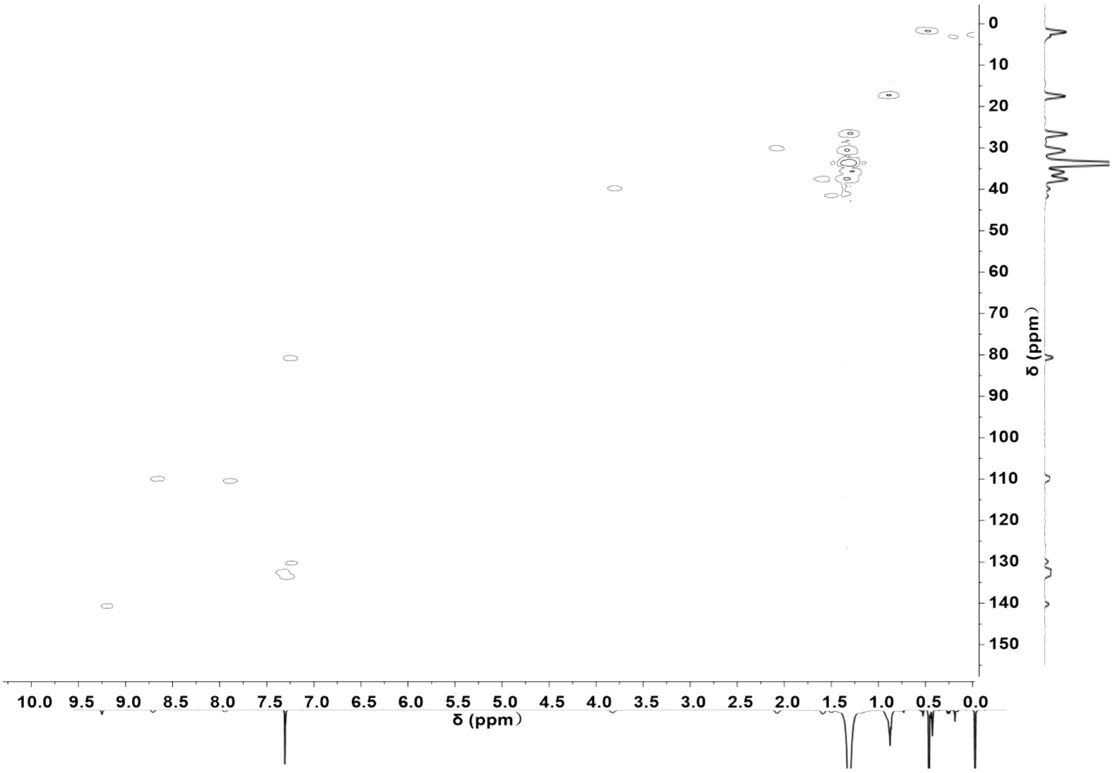


Fig. S2 Heteronuclear multiple bond correlation of BBIN-1.

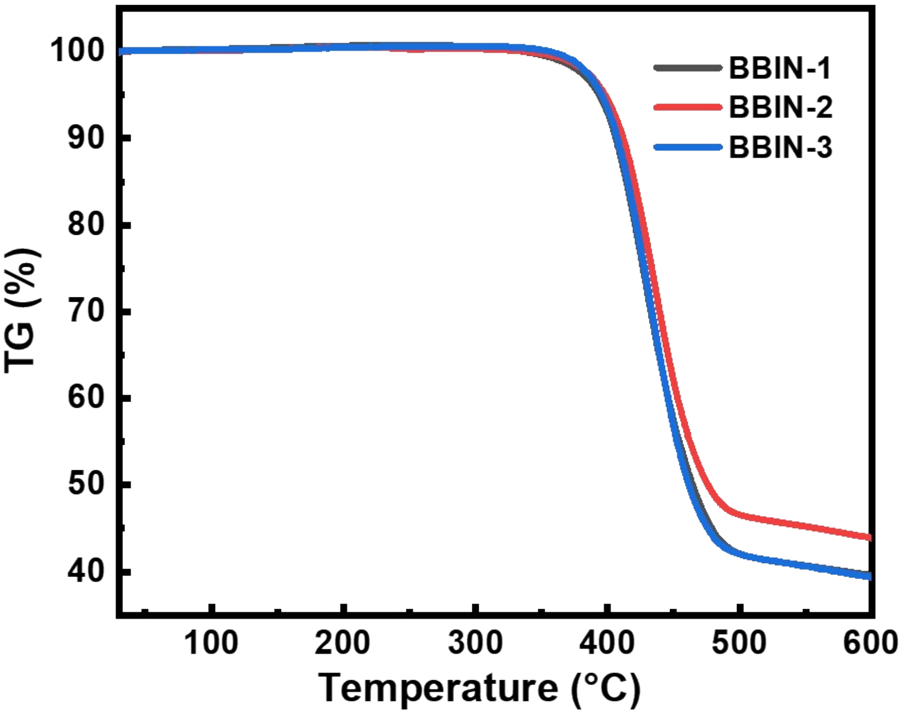


Fig. S3 Thermogravimetric analysis (TGA) of BBIN-1, BBIN-2 and BBIN-3.

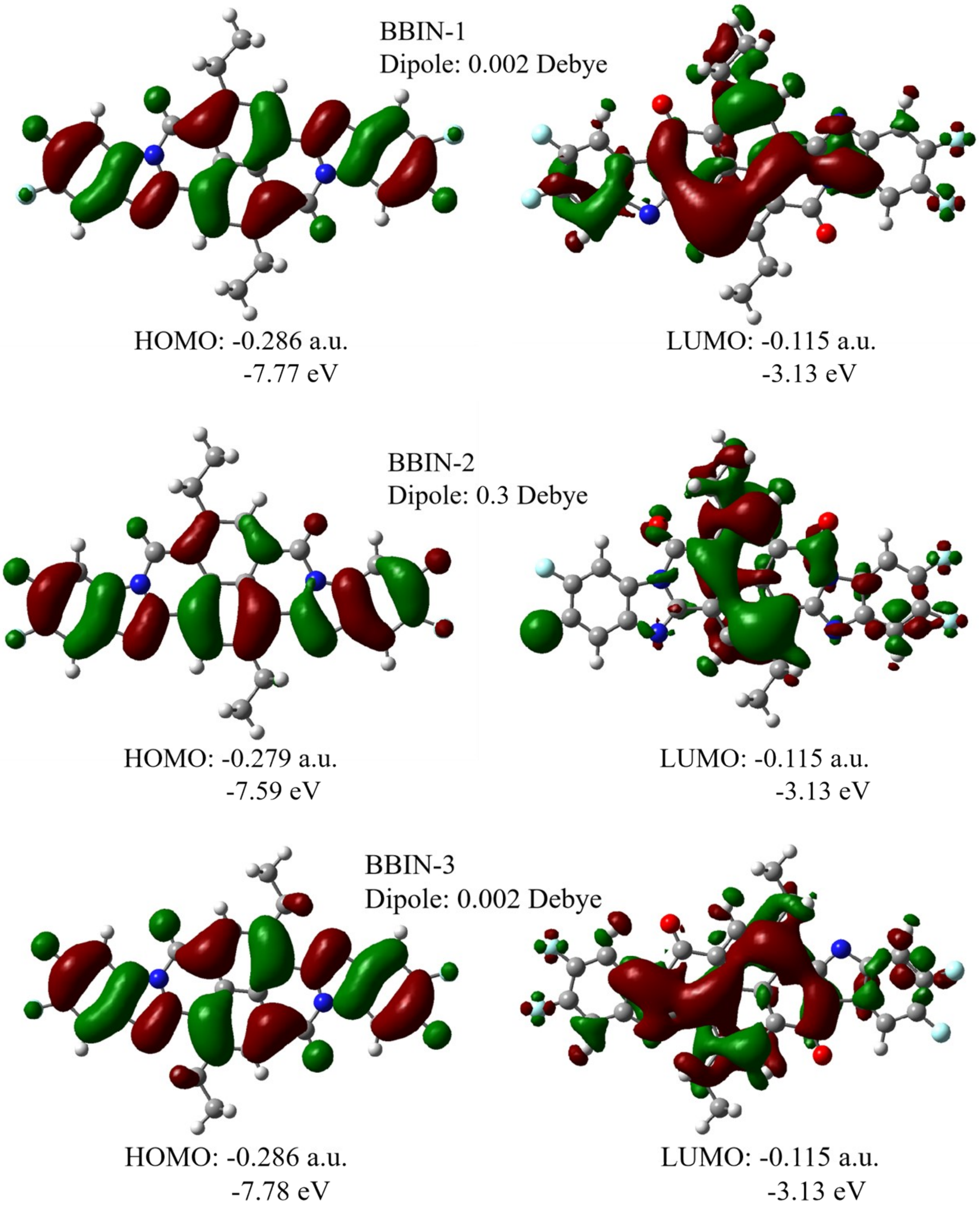


Fig. S4 DFT-calculated HOMO and LUMO surfaces and dipole moment of the optimal geometries of BBIN series at the M06-2x/6-311++g(d,p) level.In order to reduce the cost of the calculations, ethyl substituents were considered in the model compounds instead of long alkyl chains.

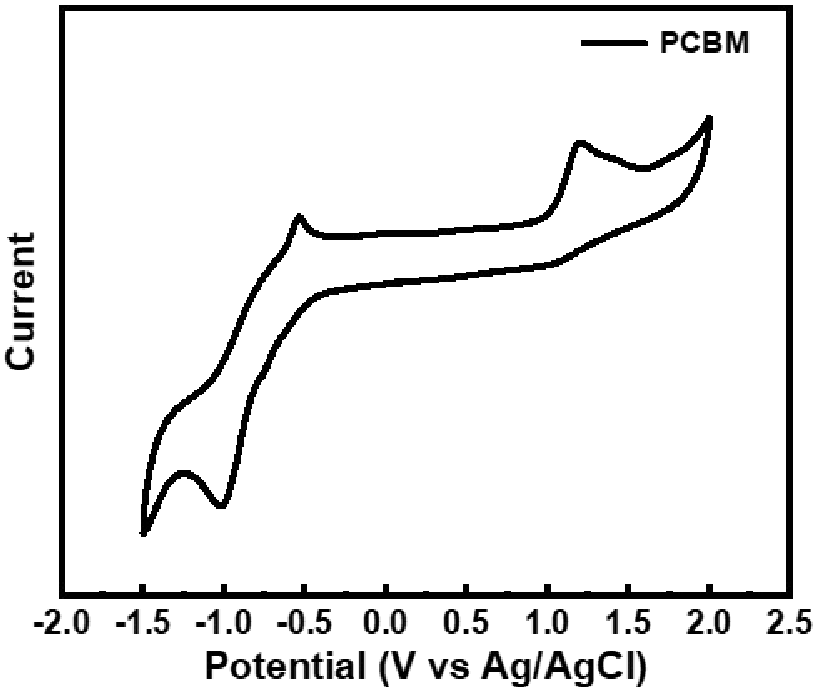


Fig. S5 CV curve of $PC_{61}BM$.

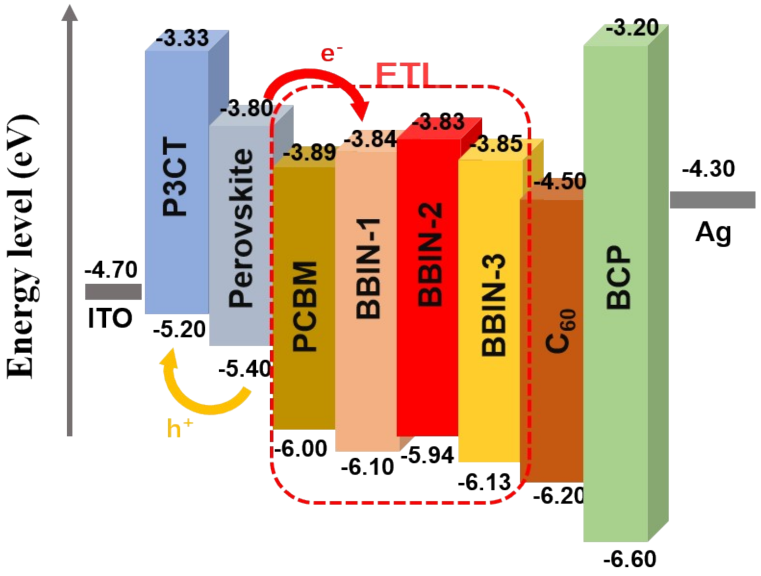


Fig. S6 Associated energy band diagrams with each component of the p-i-n PSCs.

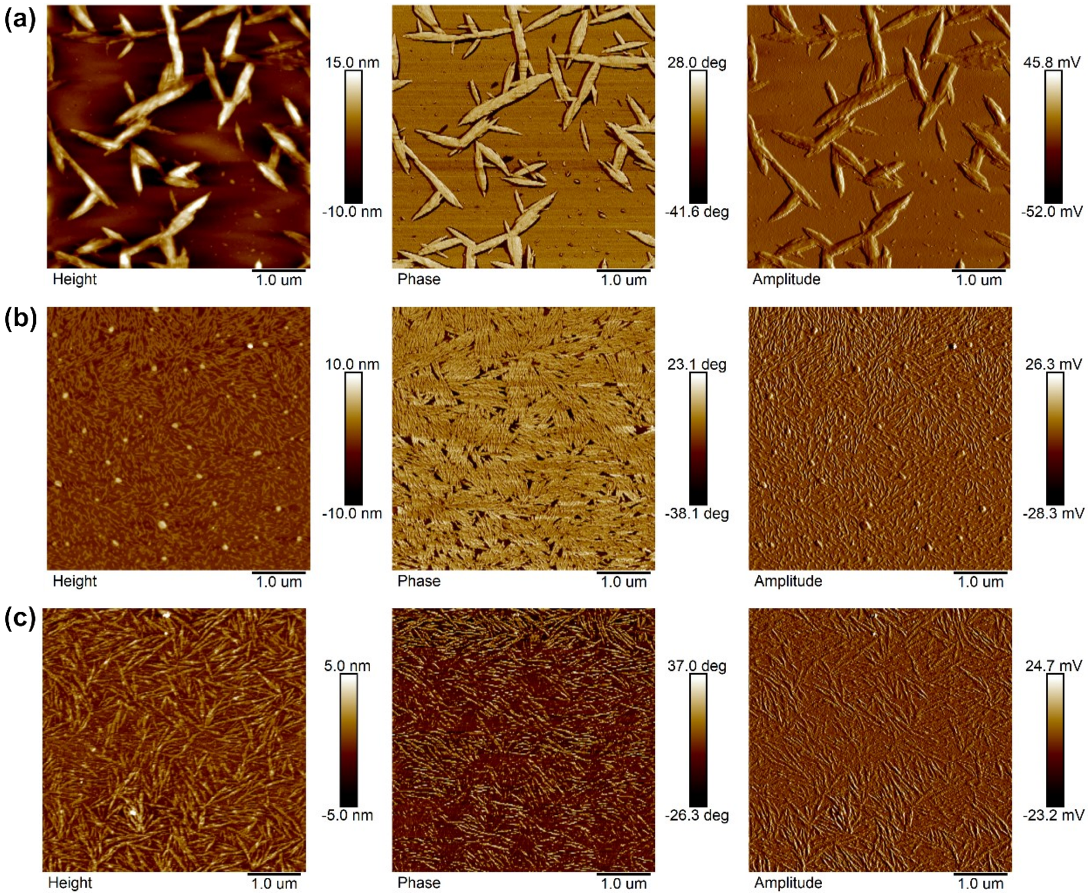


Fig. S7 AFM images of (a) BBIN-1; (b) BBIN-2; (c) BBIN-3 films deposited on bare glass substrates.

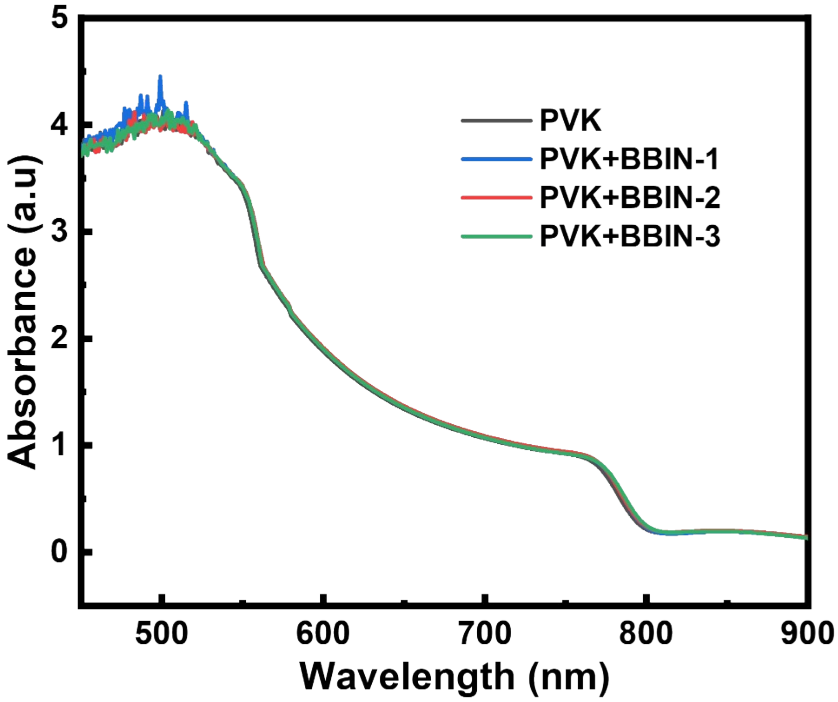


Fig. S8 UV-vis absorption spectra of perovksite with and withou BBIN series.

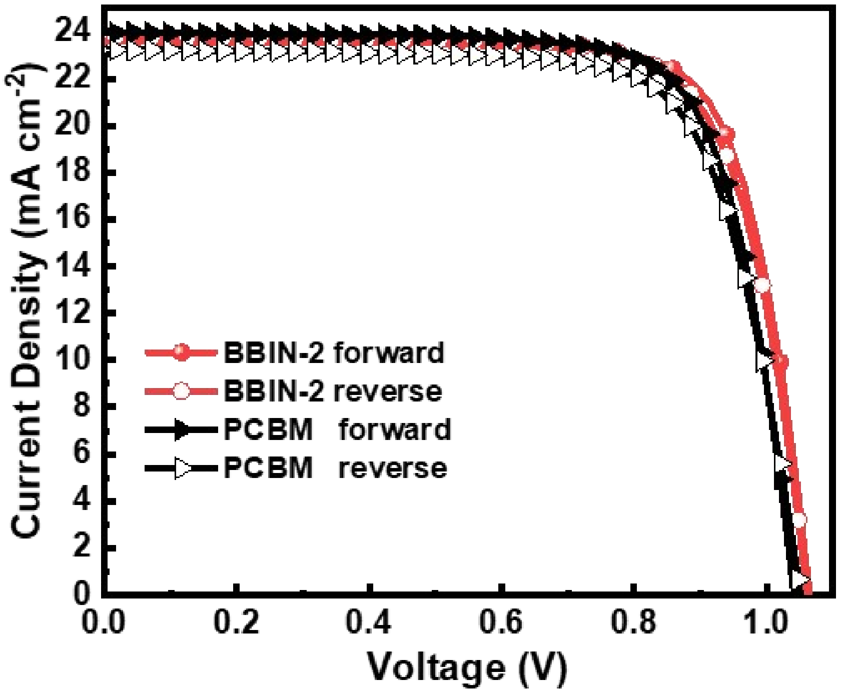


Fig. S9 J-V curves of BBIN-2 and $PC_{61}BM$ devices from forward and reverse scanning.

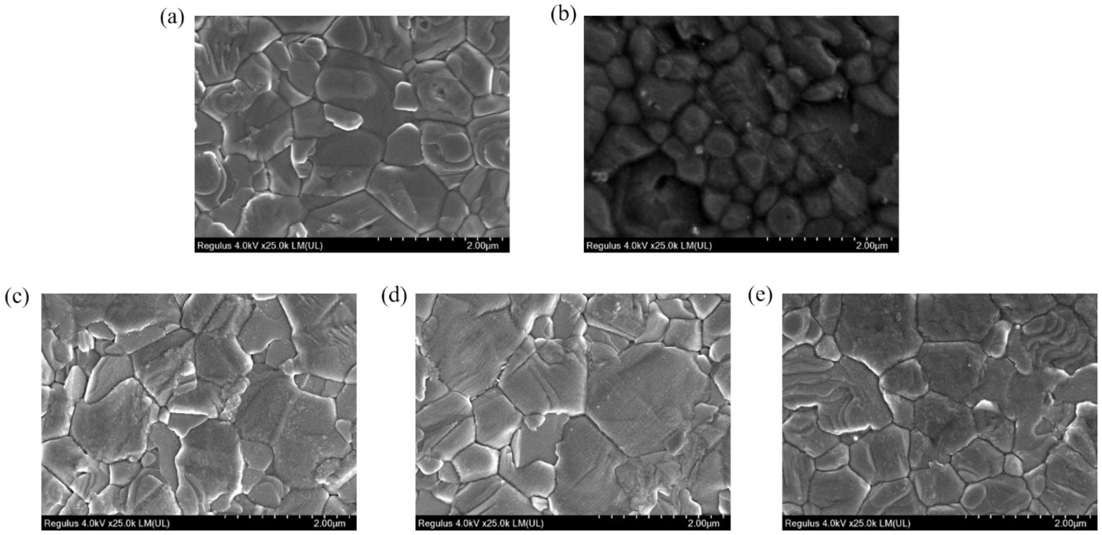


Fig. S10. SEM images of (a) CsFAPbI3, (b) CsFAPbI3/PC61BM, (c) CsFAPbI3/BBIN-1, (d) CsFAPbI3 /BBIN-2 and (e) CsFAPbI3/BBIN-3.

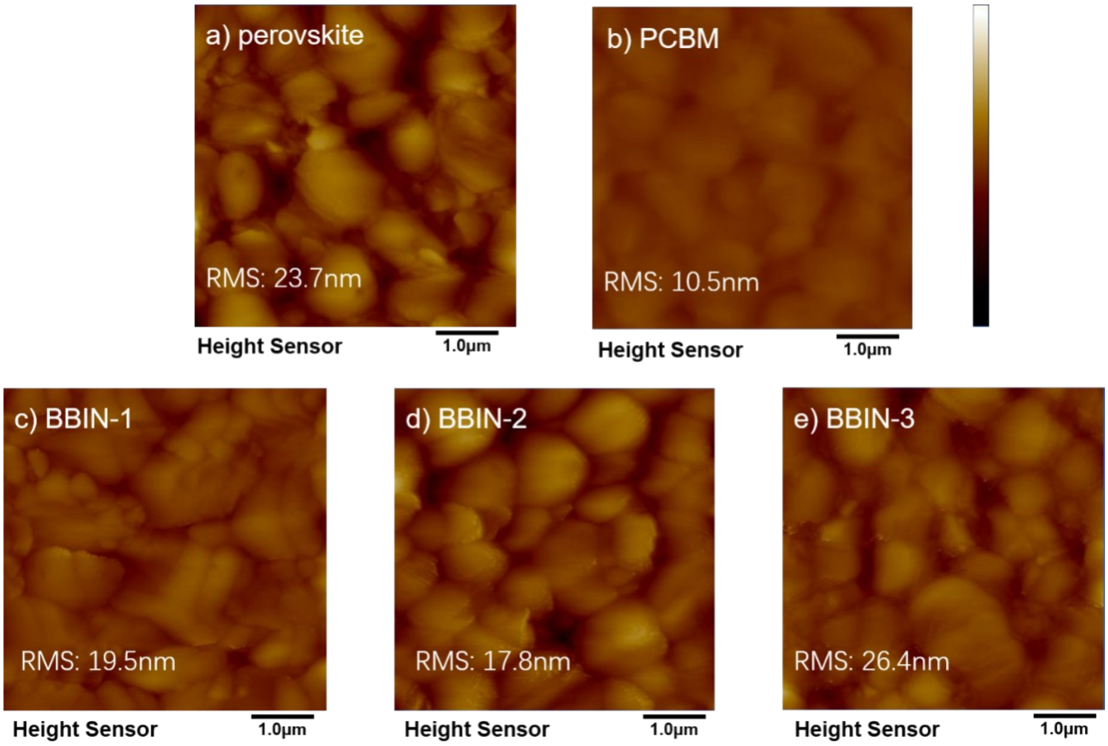


Fig. S11 AFM images of (a) CsFAPbI3, (b) CsFAPbI3/PC61BM, (c)CsFAPbI3/BBIN-1, (d) CsFAPbI3 /BBIN-2 and (e) CsFAPbI3/BBIN-3.

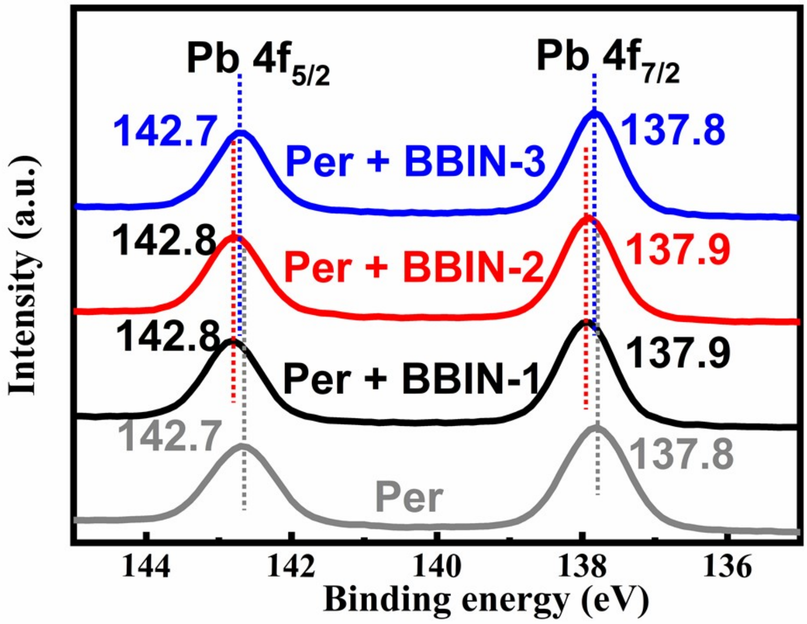


Fig. S12 High resolution XPS spectra of the Pb in the perovskite film with and without BBIN series.

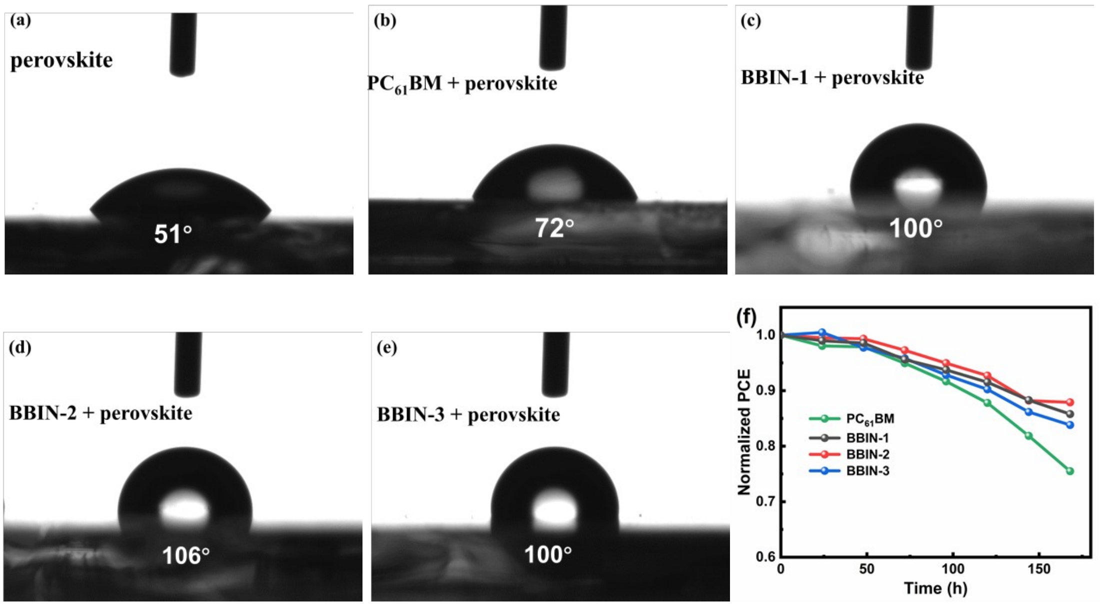


Fig. S13 Water contact angle measurements of (a) pristine perovskite film and perovskite covered by (b) PC61BM, (c) BBIN-1, (d) BBIN-2 and (e) BBIN-3. (f) Normalize PCE values of PSCs with various ETMs along with the storage time.

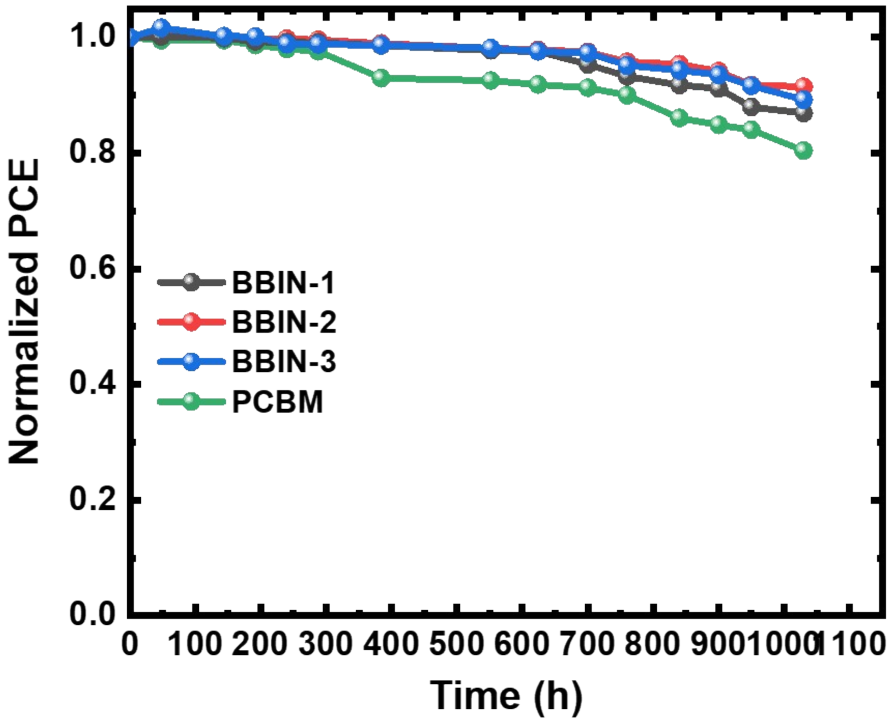


Fig. S14 Stability of BBIN series device and PC$_{61}$BM device.

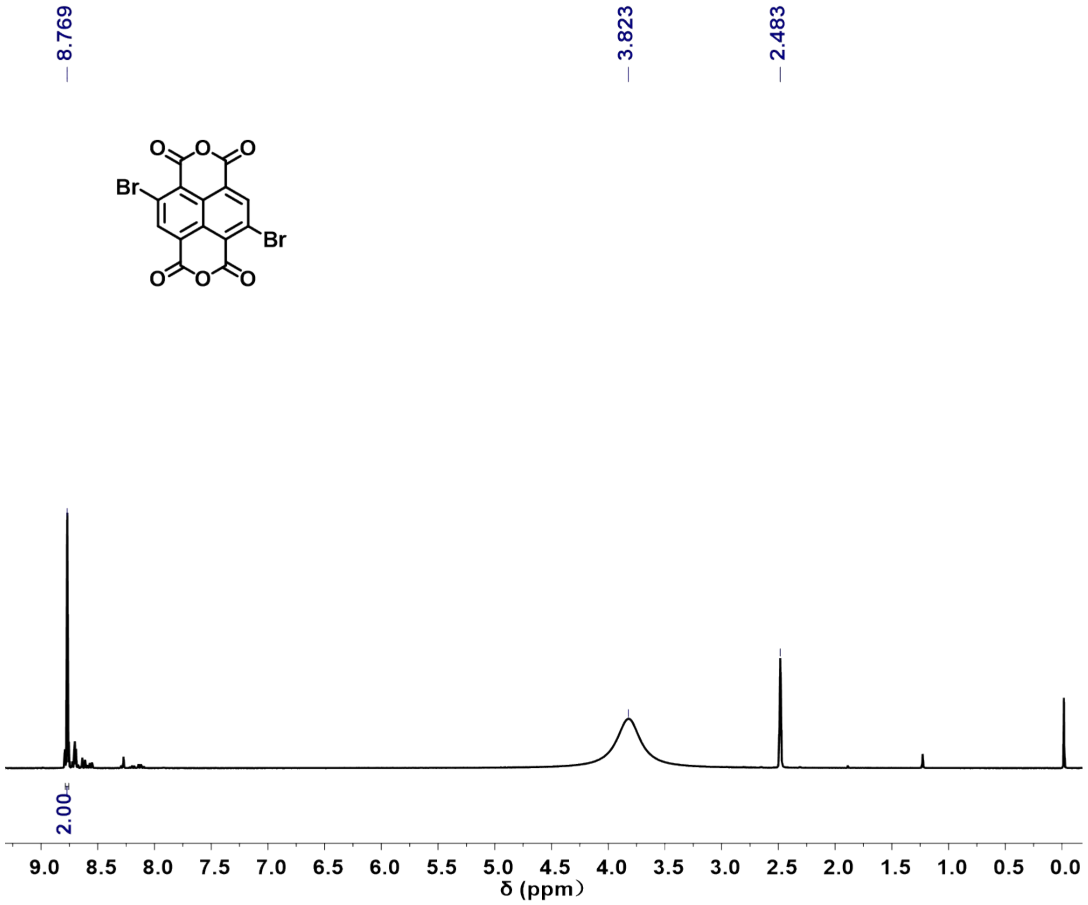


Fig. S15 ^{1}H NMR spectrum of compound **a**.

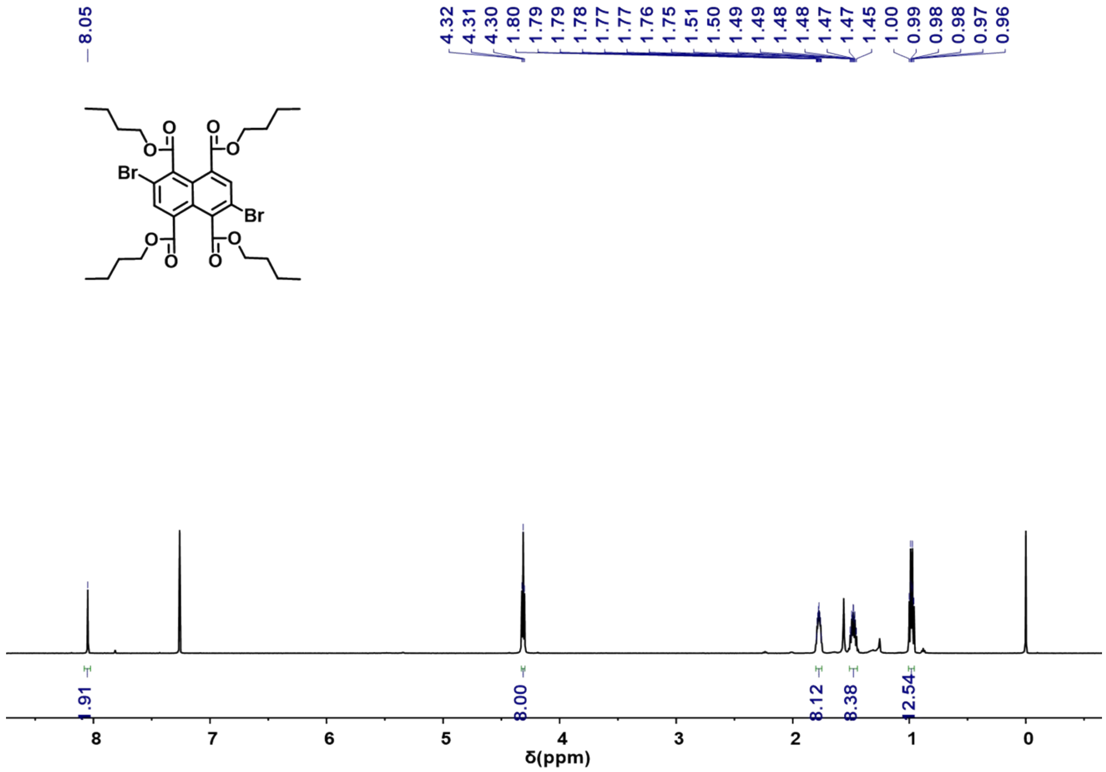


Fig. S16 ^{1}H NMR spectrum of compound **b**.

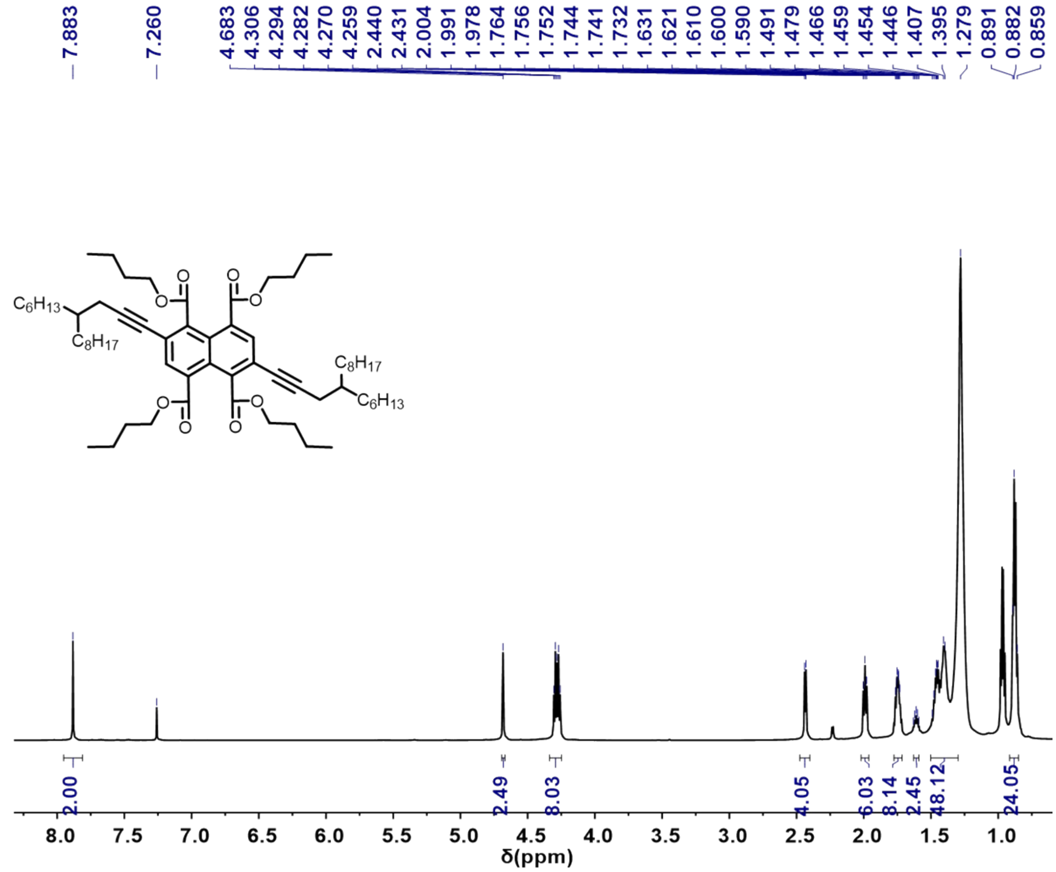


Fig. S17 ^{1}H NMR spectrum of compound **c**.

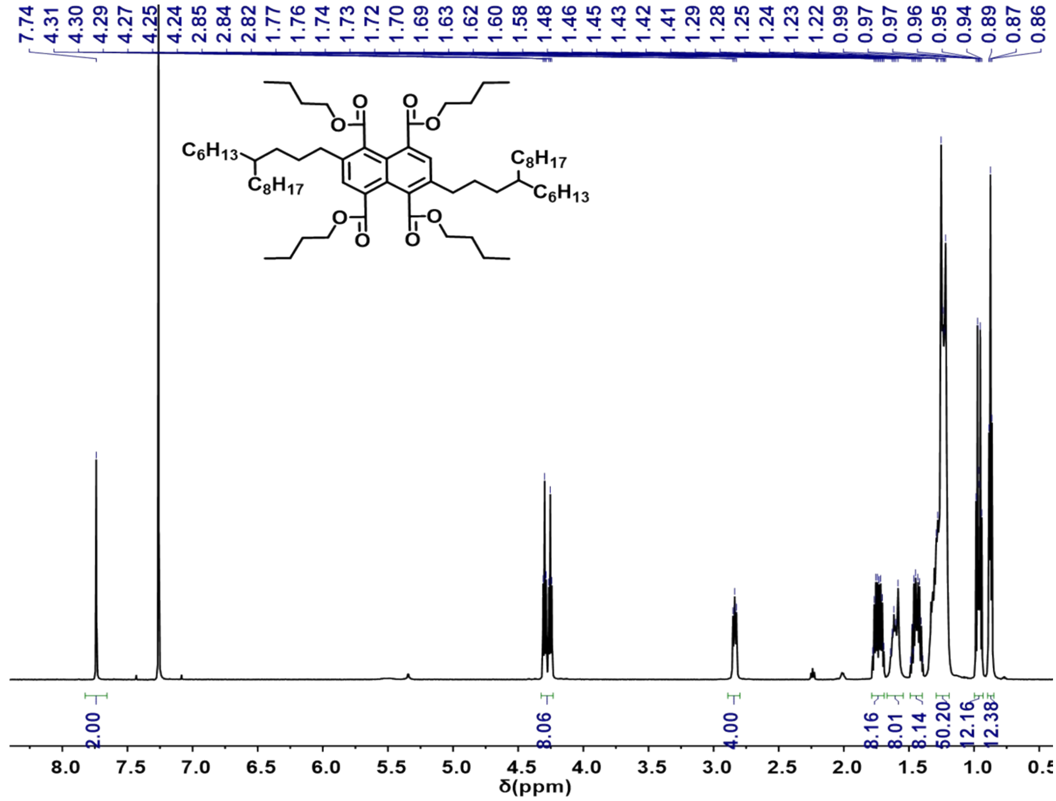


Fig. S18 ^{1}H NMR spectrum of compound **d**.

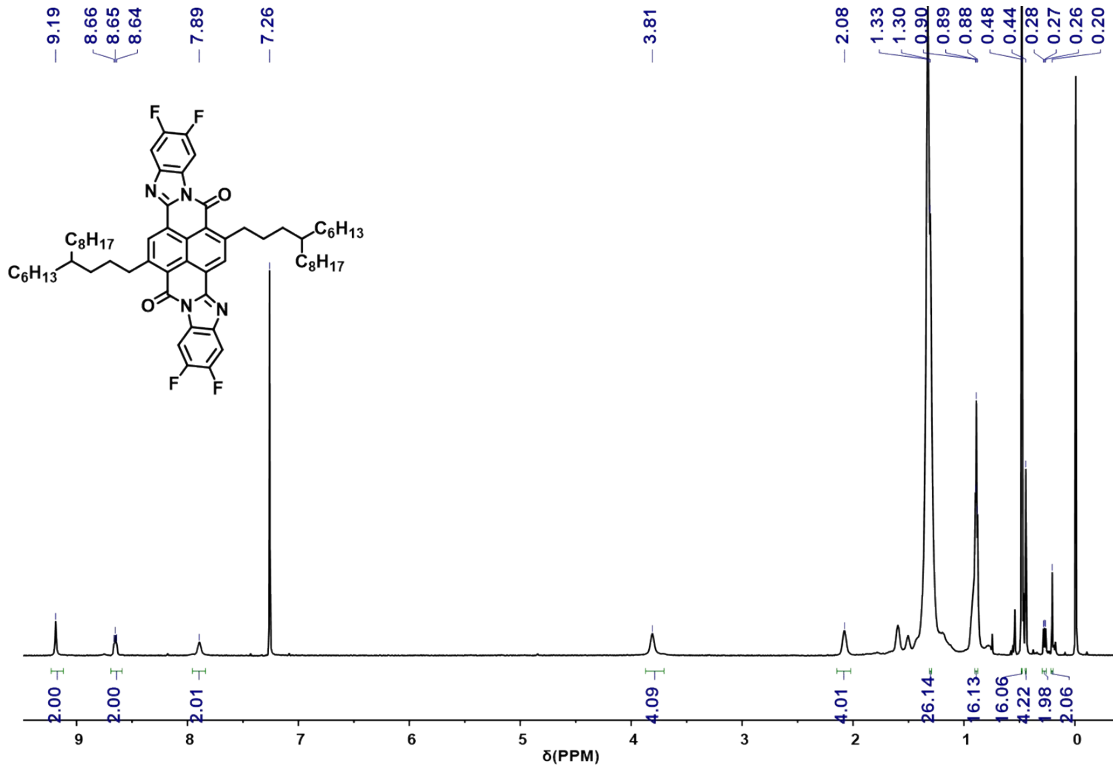


Fig. S19 ¹H NMR spectrum of compound **BBIN-1**.

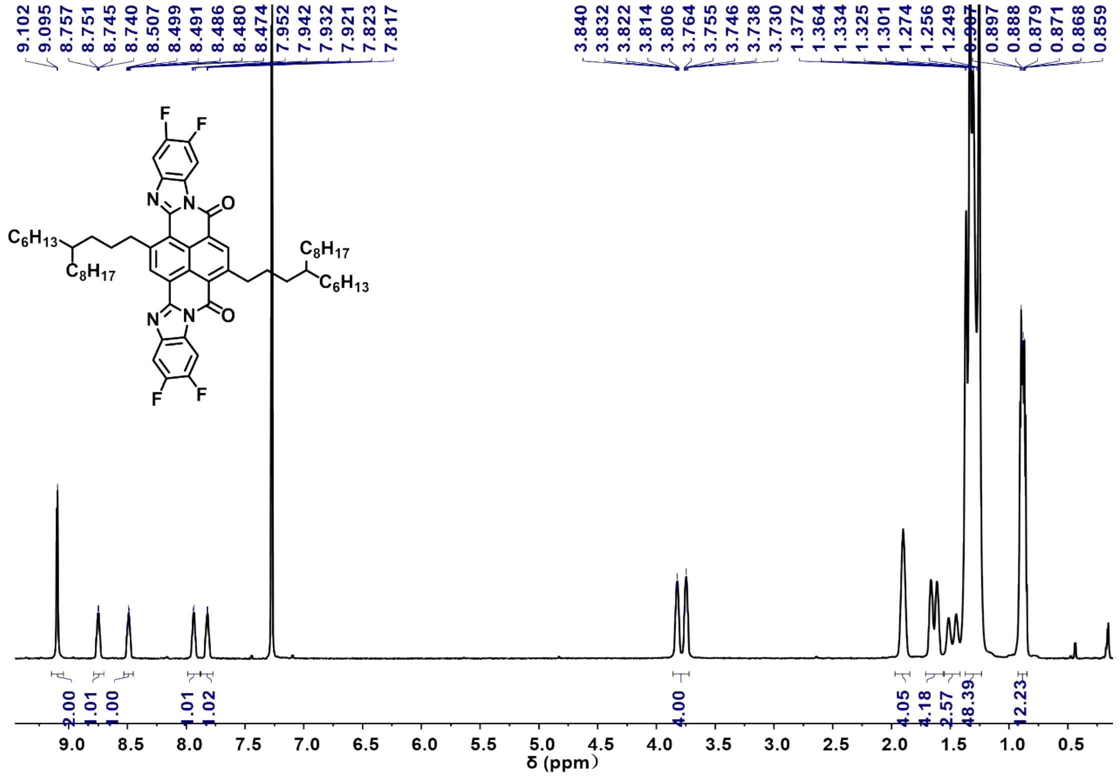


Fig. S20 ¹H NMR spectrum of compound **BBIN-2**.

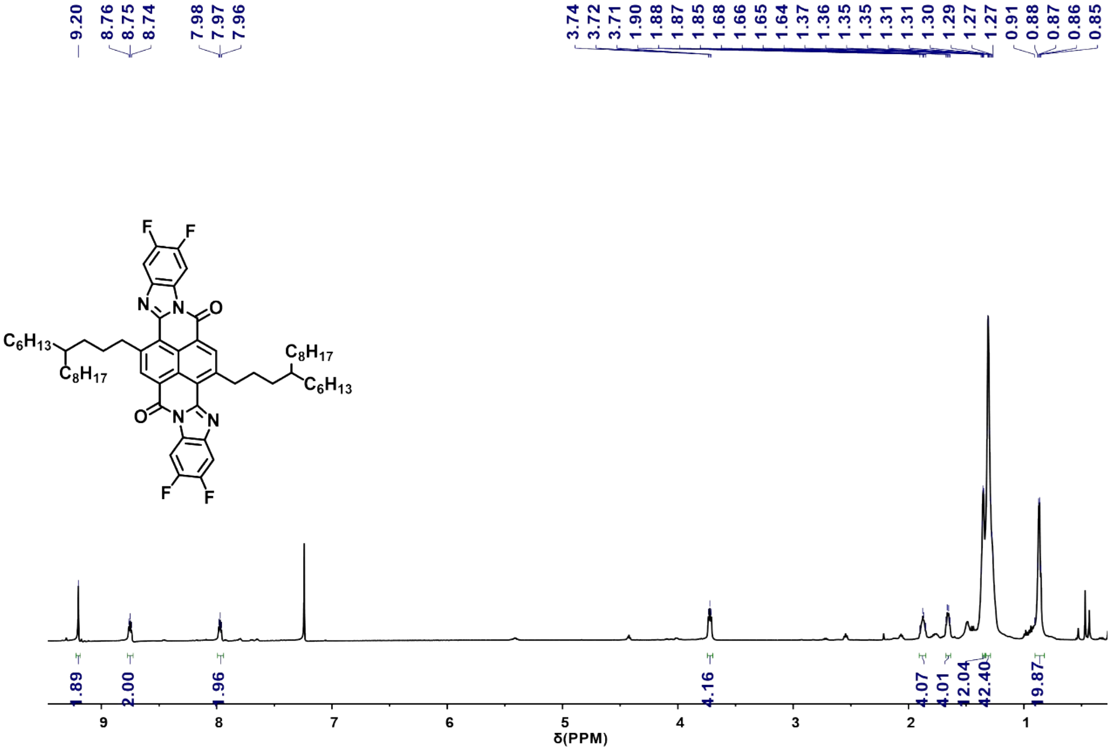


Fig. S21 ^{1}H NMR spectrum of compound **BBIN-3**.

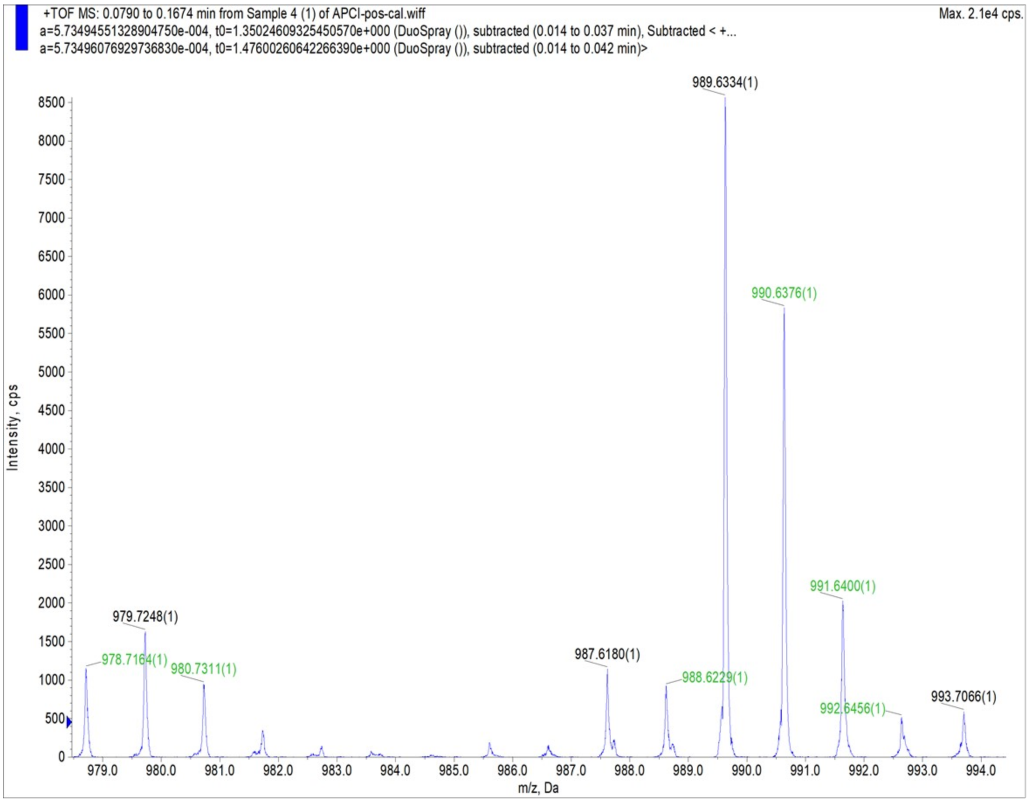


Fig. S22 Time of flight mass spectrometry of **BBIN-1**.

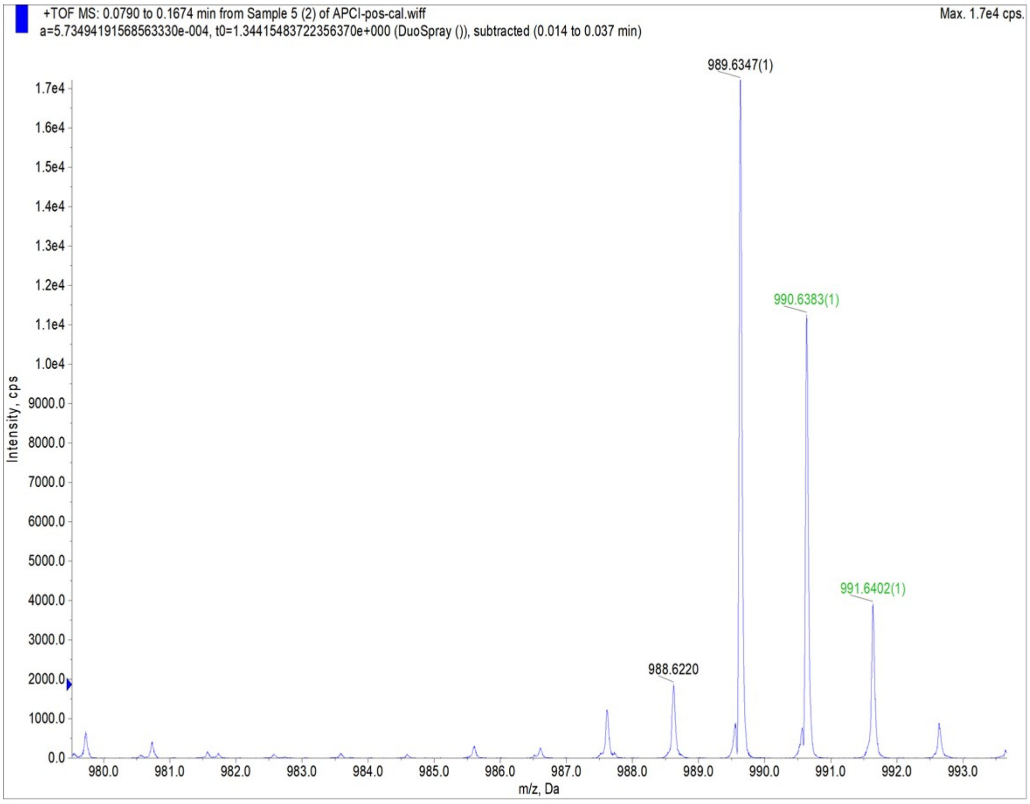


Fig. S23 Time of flight mass spectrometry of **BBIN-2**.

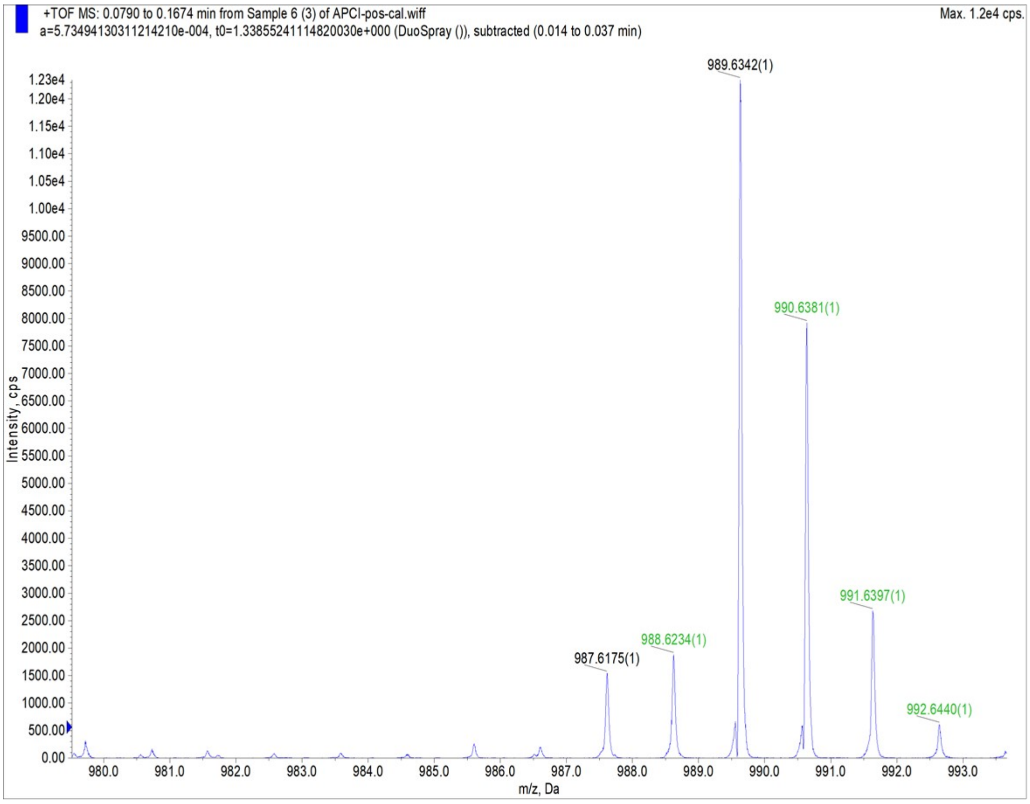


Fig. S24 Time of flight mass spectrometry of **BBIN-3**.