Supporting Information

Enhanced Performance of Perovskite Solar Cells via Construction of Benzothiadiazole-Based Hole Transport Materials Utilizing Asymmetric Strategy

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1. Experimental

1.1 Materials

Unless specified otherwise, all materials were used as received. Fluorine Doped Tin Oxide (FTO) Coated Glass (TEC; 7 Ω sq^{-1}, Advanced Election Technology Co., Ltd.), titanium diisopropoxide bis(acetylacetonate) (75% in Isopropyl Alcohol, TCI), ethanol (⩾99.5%, Aladdin), 4-Methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline, 4,7-Dibromobenzo[c]-1,2,5-

thiadiazole, Diphenylamine, Di(pyridin-4-yl)amine were obtained from Energy Chemicals, China. Lead iodide (PbI_2), Formamidinium iodide (FAI), Methylammonium Chloride (MACl), 2,2',7,7'-tetrakis[*N*, *N*-di(4-methoxyphenyl)amino]-9,9′-spirobifluorene (Spiro-OMeTAD) were purchased from Advanced Election Technology Co., Ltd., Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI) and 4-tert-butylpyridine were form Xi'an Polymer Light Technology Corp., Titanium (IV) tetraisopropoxide, Acetylacetone in isopropanol, anhydrous solvents of chlorobenzene, Dimethylformamide (DMF), Dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich. All solvents and reagents were analytical grade, without further purification.

1.2 PSCs device fabrication

The n-i-p device configuration was adopted in this study (FTO/TiO_2/SnO_2/Perovskite/B-DPT or B-TPA/Au). The patterned FTO substrate was sequentially cleaned with Hellmanex (2%, deionized water), deionized water, acetone, and isopropanol in the ultrasonic bath for 20 min, respectively. The FTO substrate was then further cleaned with Ultraviolet-Ozone surface treatment for 15 min. Compact TiO_2 layer was deposited on top of FTO glass using the spray pyrolysis method (O_2 as the carrier gas): The substrate was preheated to 450 °C; a precursor solution was diluted 0.6 mL titanium diisopropoxide bis(acetylacetonate), 75 wt % in IPA and 5.4 mL dry ethanol. Note that the spraying process must be even and dense (little and often). After spray pyrolysis, the FTO/c-TiO_2 substrate was heat at 450 °C for 1 h before cooling down to ambient temperature. The thickness of c-TiO_2 is about 20 nm. The compact SnO_2 layer was fabricated by the PAA modification method. SnO_2 colloid precursor were diluted 25 times with deionized water and then mixed with PAA (0.4 mg/mL) under stirring at 80 °C for 2 h. The resulting solution was spin-coated onto the c-TiO_2 layer at 4000 rpm (2000 rpm/s) for 30 s. The substrates were heated at 100 °C for 30 min, followed by spin-coating 10 mM KCl in deionized water at 3000 rpm (2000 rpm/s) for 30 s and annealing at 100 °C for 10 min. Before perovskite deposition, the FTO/TiO_2/SnO_2 substrate was treated by a UV-Ozone for 15 min. Finally, the substrates were transferred to the N_2 glove box (H_2O and O_2 content < 1 ppm) for perovskite layer deposition. Before coating the perovskite layer, the substrate was treated with oxygen plasma for 15 min and transferred immediately to the glove box for further process. The $FAPbI_3$ perovskite precursor solution was prepared by mixing 1.48 M PbI_2, 1.34 M FAI and 0.5 M MACl in DMF: DMSO (8:2) was spin-coated onto TiO_2 with two-step program: 1,000 and 3,000 rpm for 10 and 20 s, respectively. During the second step, 200 μL of chlorobenzene was drop-coated to treat the perovskite films. The substrate was dried on a hot plate at 150 °C for 10 min to produce $FAPbI_3$ halide perovskite thin film in a glovebox. Subsequently, the HTL was spin-coated on the perovskite layer at 3000 rpm for 30 s. The HTM solution was prepared by dissolving B-DPT or B-TPA (70 mg/mL) with and mixing it with 125 μL t-BP, 17.5 μL Li-TFSI (520 mg/mL in acetonitrile). For spiro-OMeTAD based devices, the solution was prepared by dissolving spiro-OMeTAD (90 mg/mL) with and mixing it with 39 μL t-

BP, 23 μL Li-TFSI (520 mg/mL in acetonitrile), and 10 μL tris(2-(1H-pyrazol-1-yl)-4tert-butylpyridine)-cobalt (III)tris(bis(trifluoromethylsulfonyl) imide) (FK-209) (320 mg/mL in acetonitrile). Finally, the 100 nm Au electrode was thermally evaporated on top of HTL layer to complete device fabrication process. The active area of the device is 0.09 cm^2.

1.3 Characterization

The UV-Vis absorption spectra were measured using SHIMADZU. The SEM images were taken on a JEOL JSM-7800. The light source for the photocurrent-voltage (*J-V*) measurement is an AM 1.5G solar simulator. The incident light intensity was 100 mW/cm^2 calibrated with a standard Si solar cell. The tested solar cells were masked to a working area of 0.09 cm^2. The photocurrent-voltage (*J-V*) curves were obtained by the linear sweep voltammetry (LSV) method using a Keithley 2400 source-measure unit. The measurement of the incident-photon-to-current conversion efficiency (IPCE) was performed with CEL-QPCE3000 photoelectric chemical quantum efficiency testing and analysis system. Differential pulse voltammetry (DPV) mesurements: Differential pulse voltammetry (DPV) was performed in dichloromethane with 0.1 M $TBAPF_6$ as the supporting electrolyte, an $Ag^+/AgNO_3$ electrode as the reference electrode, a carbon-glass electrode as the working electrode, a Pt electrode as the counter electrode and ferrocene/ferrocenium (Fc/Fc^+) as an internal reference with a CH Instruments electrochemical workstation (model 660 A).

1.4 Computational details

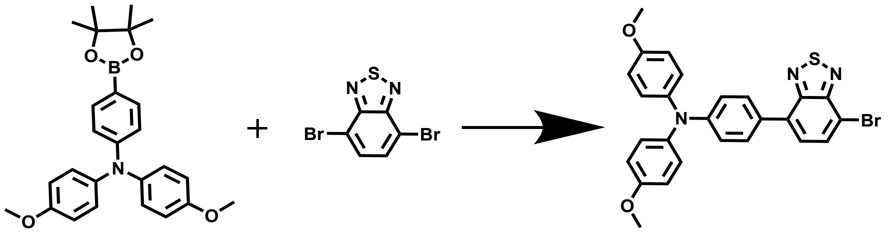
The geometry optimization and quantum chemical calculation including dipole moments and hole reorganization energy of B-DPT and B-TPA were performed by the

DFT/B3LYP method with 6-31(d, p) basis sets. All the calculations were carried out using Gaussian 06 program package.

1.5 Hole reorganization energy calculation

The internal hole reorganization energy (λ_h) can be expressed as λ_h = IP(v) – HEP, where IP(v) stands for vertical ionization potential and HEP stands for hole extraction potential. [1]

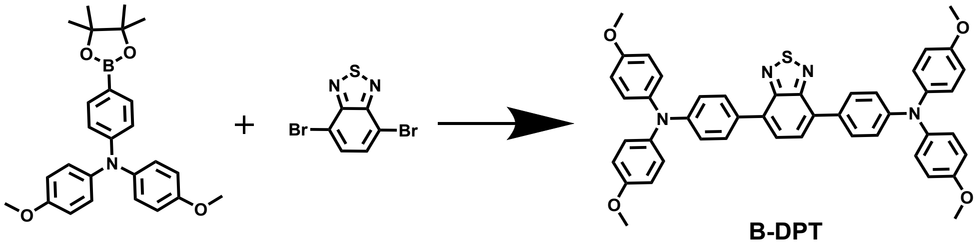
1.6 The synthetic route of B-DPT and B-TPA



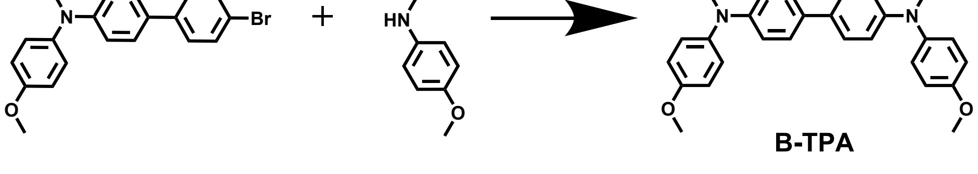
BTD-Br

The synthetic of BTD-Br: 4-Methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (431.3 mg, 1 mmol), 4,7-Dibromobenzo[c]-1,2,5-thiadiazole (291.8 mg, 1 mmol), potassium carbonate (1105.6 mg, 8 mmol), and tetrakis(tri-o-tolylphosphine)palladium(0) (115.6 mg, 0.1 mmol) were dissolved in 20 mL of toluene The mixture solution was heated and refluxed under N_2 atmosphere for 12 h. The reaction solution was poured into water, it was then extracted three times with dichloromethane and dried with anhydrous magnesium sulphate. The resulting crude product was purified by silica gel column chromatography (dichloromethane/petroleum ether = 4:1, *v*/*v*) to give yellow solid compound 1 (310 mg, 60% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.90 (d, J = 7.7 Hz, 1H), 7.79 – 7.74

(m, 2H), 7.53 (d, J = 7.7 Hz, 1H), 7.19 – 7.13 (m, 4H), 7.08 – 7.02 (m, 2H), 6.91 – 6.86 (m, 4H), 3.84 (s, 6H).



The synthetic of B-DPT: 4-Methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (953.11 mg, 2.2 mmol), 4,7-Dibromobenzo[c]-1,2,5-thiadiazole (291.8 mg, 1 mmol), potassium carbonate (2211.2 mg, 16 mmol), and tetrakis(tri-o-tolylphosphine)palladium(0) (231.2mg, 0.2 mmol) were dissolved in 50 mL of toluene The mixture solution was heated and refluxed under N_2 atmosphere for 12 h. The reaction solution was cooled to room temperature and extracted by water. The solution was dried with anhydrous magnesium sulfate. The crude product was purified by silica gel column chromatography (petroleum ether/dichloromethane = 2:1, *v*/*v*) to give a dark red solid BTD-DA (682.88 mg, 92% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.86 – 7.80 (m, 4H), 7.71 (s, 2H), 7.20 – 7.14 (m, 8H), 7.11 – 7.05 (m, 4H), 6.93 – 6.84 (m, 8H), 3.84 (s, 12H). TOF m/z: found: 742.363, calculated: $C_{46}H_{38}N_4O_4S$, 742.2614.



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The synthetic of B-TPA: The compound BTD-Br (1034.1 mg, 2 mmol), 4,4’-Dimethoxydiphenylamine (504.04 mg, 2.2 mmol), palladium acetate (44.9 mg, 0.2 mmol), tri-tert-butylphosphine (809.3 mg, 0.4 mmol) and sodium tert-butoxide (576.6 mg, 6 mmol) were dissolved in 50 mL of toluene and the mixture solution was reacted under N_2 atmosphere at 120 °C for 10 h. The reaction solution was cooled to room temperature and extracted by water. The solution was dried with anhydrous magnesium sulfate. The crude product was purified by silica gel column chromatography (petroleum ether/dichloromethane = 2:1, v/v) to give a dark red solid BTD-DA (1279.16 mg, 96% yield). ^{1}H NMR (400 MHz, DMSO-d6) δ 7.79 – 7.73 (m, 2H), 7.62 (d, J = 7.8 Hz, 1H), 7.11 – 7.04 (m, 4H), 6.99 – 6.91 (m, 9H), 6.89 – 6.82 (m, 6H), 3.75 (s, 6H), 3.73 (s, 6H). TOF m/z: found: 666.296, calculated: $C_{40}H_{34}N_4O_4S$, 666.2301.

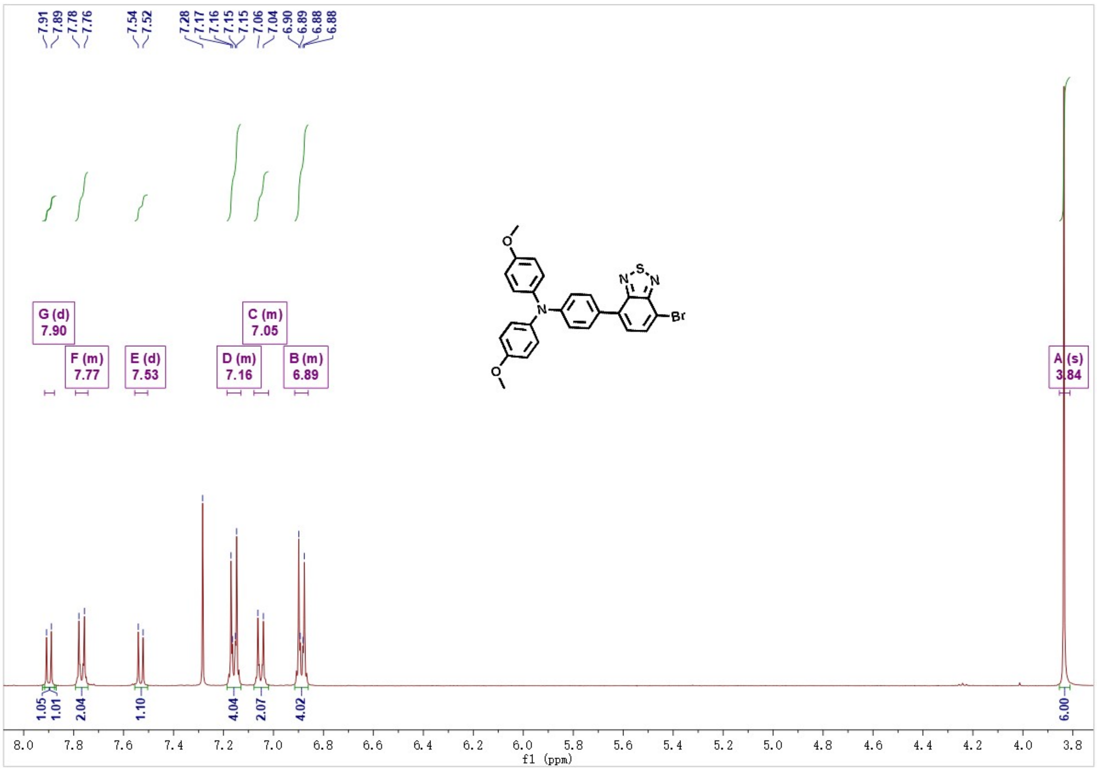

Figure S1. The ^{1}H NMR of BTD-Br.

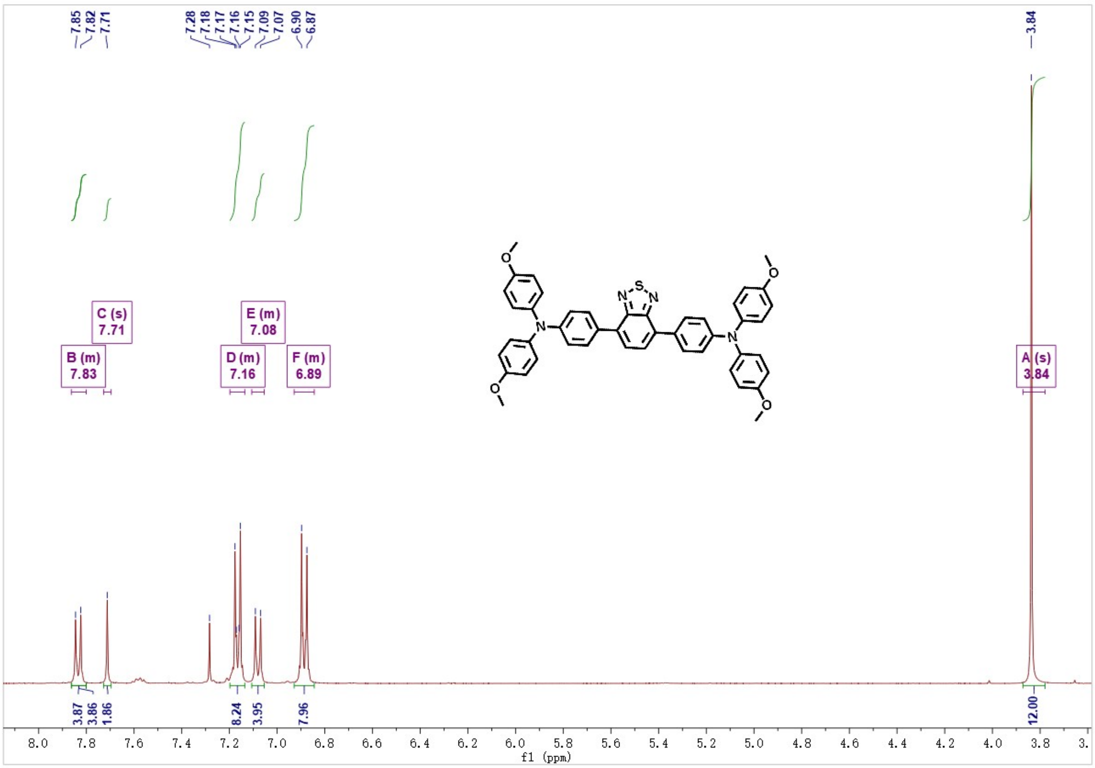

Figure S2. The ^{1}H NMR of B-DPT.

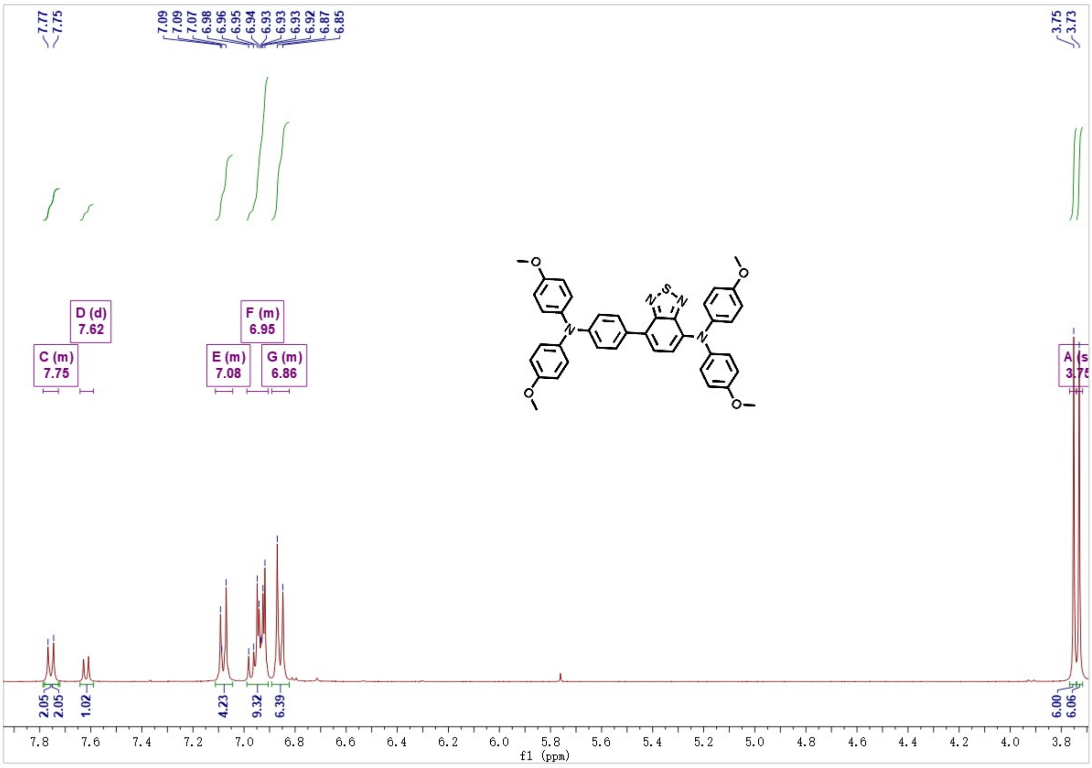

Figure S3. The ^{1}H NMR of B-TPA.

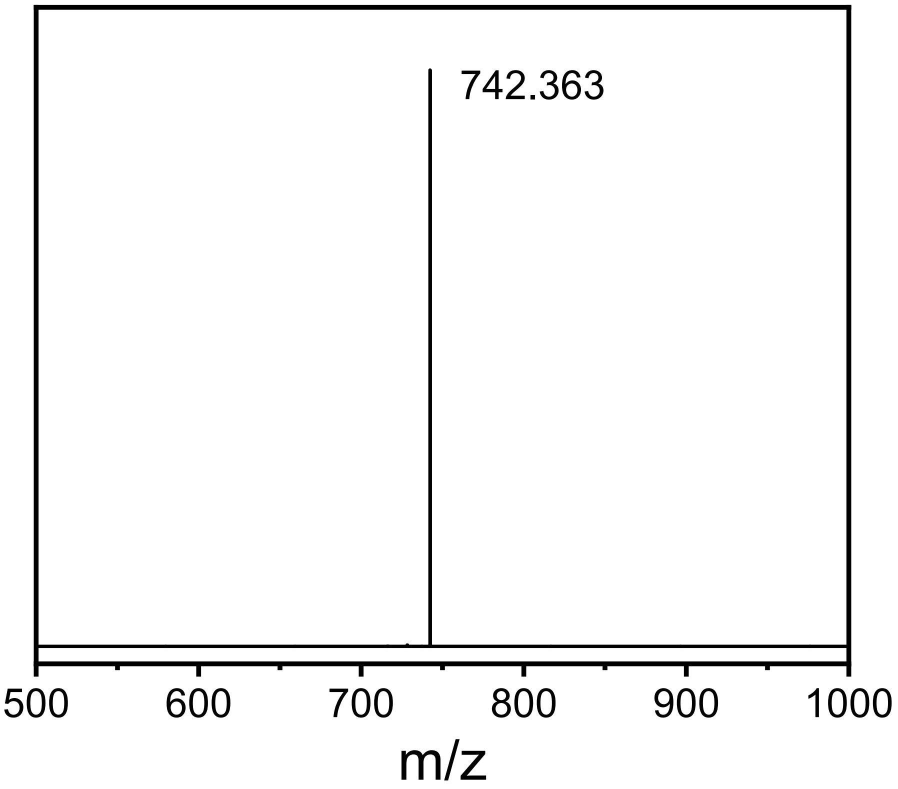

Figure S4. The TOF of B-DPT.

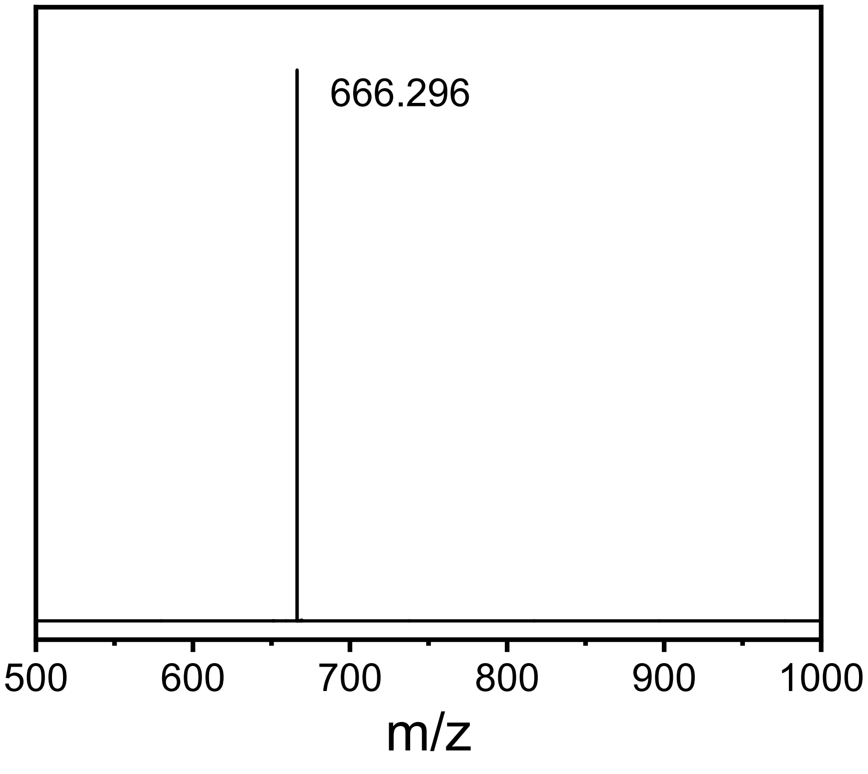

Figure S5. The TOF of B-TPA.

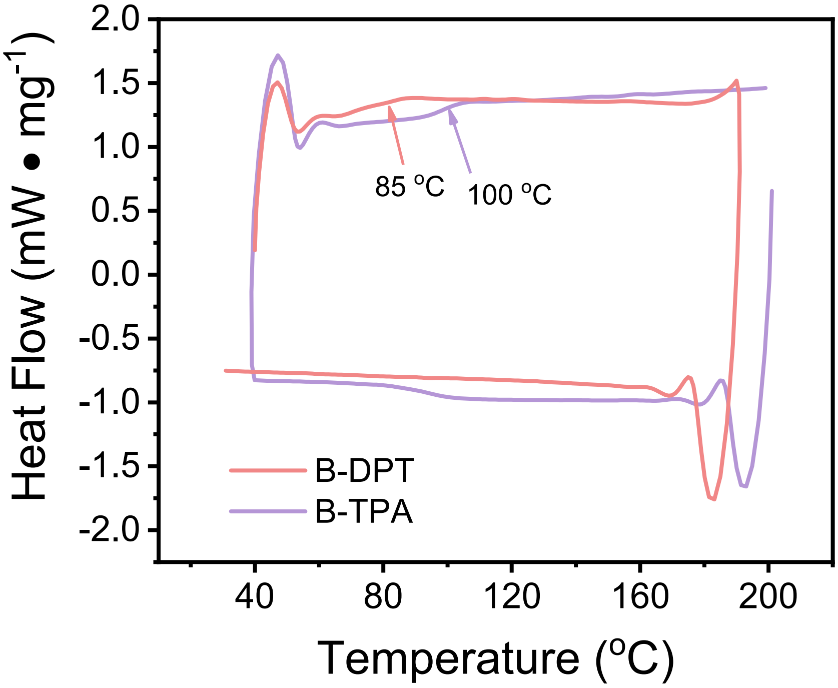

Figure S6. DSC curves of B-DPT and B-TPA.

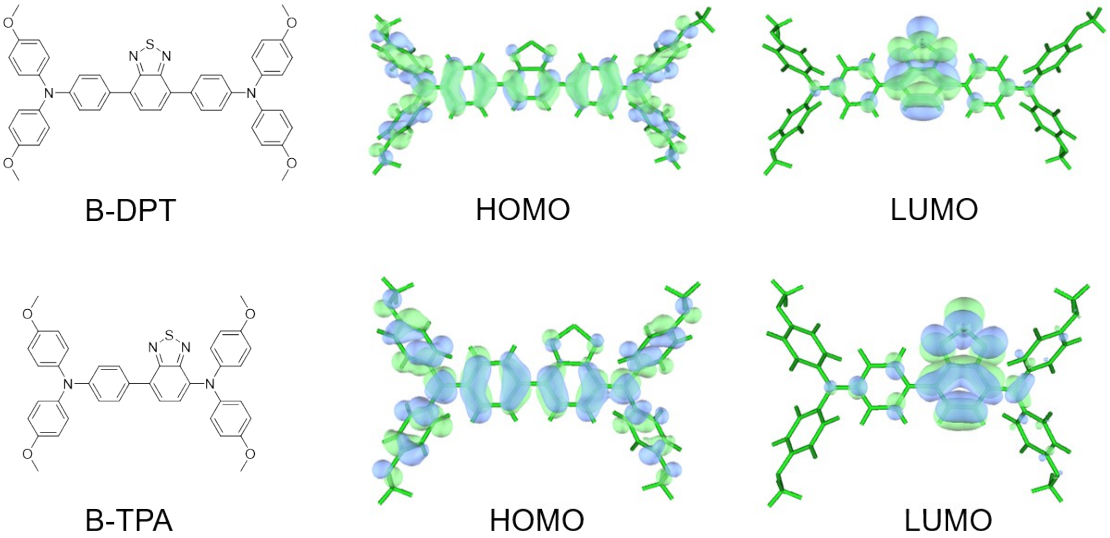

Figure S7. DFT calculated HOMO/LUMO energy levels of B-DPT and B-TPA.

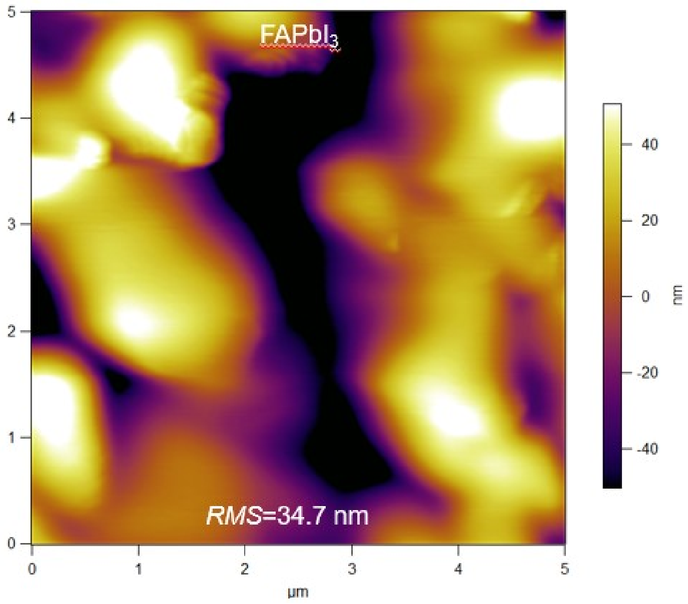

Figure S8. 2D AFM of perovskite.

Table S1. Detailed estimation of the total cost for 1 g B-TPA HTM based on the calculated materials quantities as illustrated in synthetic route.

Chemicals	**Price**	**Dosage**	**Cost (RMB)**
4-Methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline	1 g / 80 RMB	1.13 g	90.4
4,7-Dibromobenzo[c]-1,2,5-thiadiazole	1 g / 5 RMB	0.76 g	3.8
bis(4-methoxyphenyl)amine	1 g / 7 RMB	0.36 g	2.52
P(t-Bu)$_3$	1 g /5.75 RMB	0.067 g	0.38

K_2CO_3	500 g /20 RMB	3 g	0.12
$Pd(PPh_3)_4$	10 g /430 RMB	0.15 g	6.45
$Pd(OAc)_2$	1 g /369.13 RMB	0.02 g	7.4
t-BuONa	1 g/ 0.064 RMB	0.48 g	0.03
Na_2SO_4	500 g / 20 RMB	200 g	8
toluene	500 mL / 30 RMB	250 ml	15
DCM	1 L / 12 RMB	1 L	12
PE	1 L / 12 RMB	500 mL	6
Silica Gel	1 kg /30 RMB	300 g	9
Total			**342.41(161.1 RMB / g) (~22.53 $)**

Table S2. Comparison of synthetic cost and commercial prices of B-TPA with the representative HTMs for PVSCs.

HTM	**SpiroOMeTAD**	**PTAA**	**P3HT**	**B-TPA**
Material Costs ($/g)	91.67[2]	-	-	47.96
Commercial	170-475[3]	423.3[4]	500[5]	-

price/g

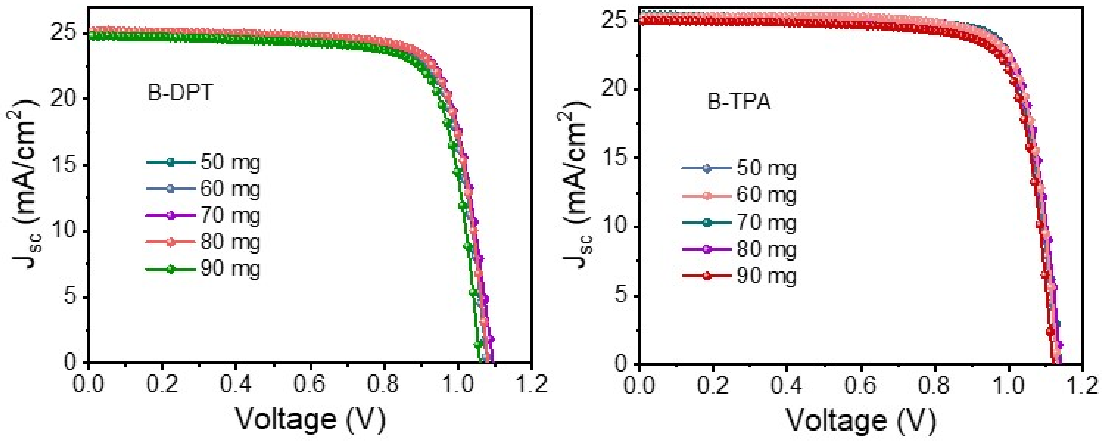

Figure S9 J-V curves of B-DPT or B-TPA modified PSCs with different concentrations.

Table S3 Photovoltaic data obtained from B-DPT modified device PSCs with different concentrations.

Concentration(mM)	Voc (V)	Jsc (mA/cm^2)	FF (%)	PCE (%)
50	1.08	24.82	76.48	20.50
60	1.08	24.96	77.07	20.77
70	1.09	25.00	77.34	21.07
80	1.08	25.03	76.96	20.81
90	1.06	24.88	76.75	20.43

Table S4 Photovoltaic data obtained from B-TPA modified device PSCs with different concentrations.

Concentration(mM)	Voc (V)	Jsc (mA/cm^2)	FF (%)	PCE (%)
50	1.13	25.26	78.1	22.29
60	1.13	25.33	79.6	22.78
70	1.14	25.42	80.06	23.20
80	1.14	25.17	79.1	22.69
90	1.12	25.04	78.8	20.10

Table S5. The TRPL parameters form B-DPT and B-TPA PSCs.

HTM	**A_1 (%)**	**τ_1 (ns)**	**A_2 (%)**	**τ_2 (ns)**	**τ**
B-DPT	90.52	2.70	9.48	63.97	8.50
B-TPA	83.32	2.51	16.68	48.59	2.17

Supporting Information

Reference

[1] K. Yang, Q. Liao, J. Huang, Z. Zhang, M. Su, Z. Chen, Z. Wu, D. Wang, Z. Lai, H. Y. Woo, Y. Cao, P. Gao, X. Guo, *Angew. Chem. Int. Ed.* **2022**, 61, e202113749.

[2] L. Chen, B. Zhang, Y. Cheng, Z. Xie, L. Wang, X. Jing, F. Wang, *Adv. Funct. Mater*. **2010**, 20, 3143

[3] M. L. Petrus, T. Bein, T. J. Dingemans, P. Docampo, *J. Mater. Chem. A* **2015**, 3, 12159.

[4] J. Zhang, Q. Sun, Q. Chen, Y. Wang, Y. Zhou, B. Song, N. Yuan, J. Ding, Y. Li, *Adv. Funct. Mater.* **2019**, 29, 1900484.

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