Supporting Information

Fluorinated Interfacial Layers in Perovskite Solar Cells: Efficient Enhancement of the Fill Factor

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Materials

All chemicals were used without extra purification unless otherwise indicated. $Pd(OAC)_2$, *tert*-butylphosphine, sodium *tert*-butoxide, sodium hydride, 5-bromo-1,2,3-trifluorobenzene, hexafluorobenzene, anhydrous toluene and tetrahydrofuran, chlorobenzene and dichloromethane were purchased from Sigma Aldrich, Alfa Aesar, Fisher scientific or Fluka and used as received. N^3,N^3,N^6,N^6-tetrakis(4-methoxyphenyl)-9-*H*-carbazole-3,6-diamine was purchased from Ikamba Organics. FTO glasses (FTO, 7 Ω per square) were purchased from Yingkou You Xuan Trade Co. Ltd. $SnCl_2 \cdot 2H_2O$ (Alfa Aesar) were used as received. Methylammonium iodide(MAI), lead iodide (PbI_2 99%) (Yingkou You Xuan Trade Co. Ltd.), dimethyl formamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.9%). 2,2′,7,7′-tetrakis(*N*,*N*-di-p-methoxyphenylamine)-9,9- spirobifluorene (spiro-OMeTAD), bis(trifluoromethanesulfonyl)imide (Li-TFSI), tert-butylpyridine (t-BP), (Sigma-Aldrich), chlorobenzene (CB, 99.8%). Acetonitrile, ethanol, isopropanoland, butanol, and isobutanol were purchased from Sigma- Aldrich without further purification.

Device Fabrication

Solutions Preparation

The perovskite precursor solution was prepared by 0.922g PbI_2 and 0.32g MAI in the mixed solvent of DMF and DMSO (7:3 v/v). Spiro-OMeTAD solution was prepared by dissolving 0.072g spiro-OMeTAD into 1 ml chlorobenzene, with the dopant of 18 μL Li-TFSI solution (520 mg in 1 mL acetonitrile), 29 μL tBP. Both of the perovskite precursor and spiro-OMeTAD solutions were prepared in glovebox, and stirred about four to five hours at room temperature. Solutions of interfacial layers: Add the solid powers of three small molecules in chlorobenzene to make a solution of 10 mg per ml, then stirred the F4BnCz2 solution at 60℃ until dissolved while the other two at room temperature.

Perovskite Solar Cells Fabrication

Cleaning the substrates (FTO) ultrasonically with detergent, deionized water and isopropanol,100w for 15 min, sequentially. Then before deposing SnO_2 as ETL, all substrates were further cleaned by UV-Ozone for 10 min. Then spin-coating SnO_2 solution immediately on FTO substrates at 500rpm for 3s and 3000 rpm for 30 s, followed by thermal annealing at 150 °C for 1 h to make the solvent completely

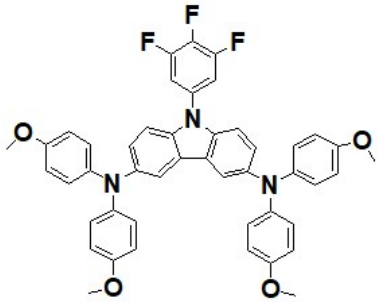
evaporate. Next, the $MAPbI_3$ precursor solution was spin-coated on FTO/SnO_2 substrates at 500 rpm for 3 s and 4000 rpm for 30 s, with quick dripping of 420 μL chlorobenzene onto the rotating perovskite film at the beginning of 9–10 s of the second spin-coating step, then annealed at 100 °C for 10 min. After cooling down, 20μL interfacial layer solutions were spin-coated onto the perovskite layer at 500 rpm for 3 s and 5000 rpm for 30 s. Put it still for a while to make sure the solvent evaporates, afterwards, 20 μL spiro-OMeTAD solution was spin-coated onto the perovskite layer at 500 rpm for 3 s and 3000 rpm for 30 s. Finally, 130 nm thick Ag electrode was thermally evaporated on top of the cells at a constant evaporation rate of 1 $Å \cdot s^{-1}$. The active area of all devices was 0.07 cm^2 defined by a metal mask.

Characterization

NMR spectra were recorded on a Bruker Avance 300 (300 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm). Mass spectra were recorded on a Finnigan MAT 8500 using an ionization energy of 70 eV (electron impact). UV-Vis absorption spectra were recorded with a Jasco V-670 spectrometer. Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC-4000 (heating/cooling rate 20°C.min^{-1}). Thermogravimetric analysis (TGA) was fulfilled using a Perkin Elmer STA 6000 at a heating rate of 10°C.min^{-1} under N_2. Cyclic voltammetry was performed on a Biologic Applied Research MPG2 multi-channel potentiostat, in a 10^{-3} mol.L^{-1} solution with 0.1 M tetrabutylammoniumperchlorate (TBAP) in dichloromethane as supporting electrolyte at a scan rate of 50 mV.s^{-1} in a three-electrode cell using platinum disk as working electrode, a platinum wire as counter-electrode, a silver wire as reference electrode and ferrocene as internal reference. The morphology and microstructures were investigated by FE-SEM (ZEISS Ultra-55). The J–V characteristics of the devices were measured with a Keithley 2440 source under a simulated AM1.5G spectrum. With a solar simulator (Newport, 91160), the light intensity was calibrated using a standard silicon solar cell device by the NREL. The external quantum efficiency (EQE) curves were measured using a standard EQE system (Newport 66902), consist of a xenon light source, a monochromator, and a potentiostat. The electrochemical impedance spectroscopy (EIS) measurements were performed on the Zahner Zennium electrochemical workstation with an illumination of 300 W m^{-2} light source. Steady-state photoluminescence emission spectroscopy (PL) was

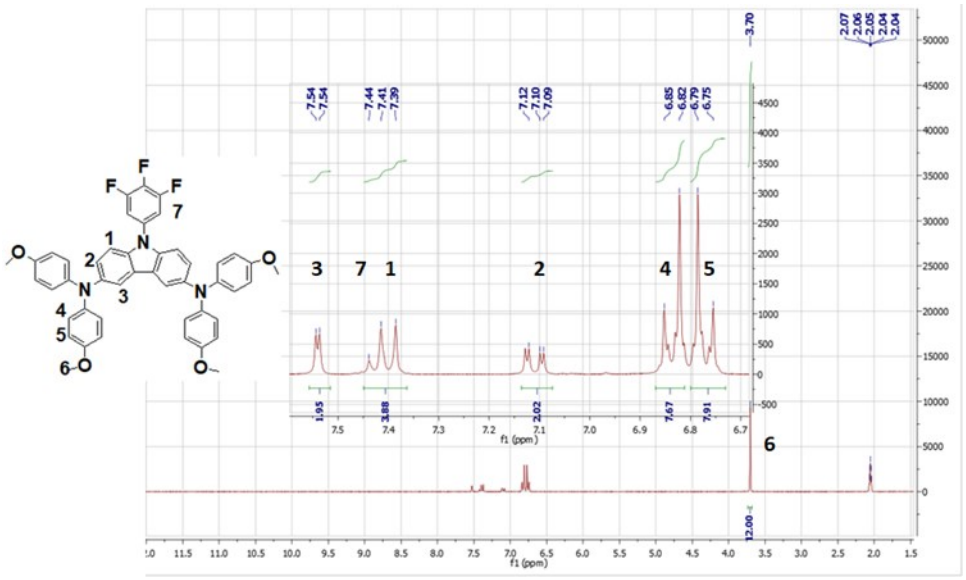
measured by fluorescence spectrometer (HITACHI F-5000) with the excitation wavelength of 450 nm.

Synthesis



***N*³,*N*³,*N*⁶,*N*⁶-tetrakis(4-methoxyphenyl)-9-(3,4,5-trifluorophenyl)-9H-carbazole-3,6-diamine (F3BnCz).**

*N*³,*N*³,*N*⁶,*N*⁶-tetrakis(4-methoxyphenyl)-9-*H*-carbazole-3,6-diamine **(3,6-CzDMPA)** (400 mg , 0.64 mmol), 5-bromo-1,2,3-trifluorobenzene **(1)** (150 mg, 0.70 mmol), NaO*t*Bu (185 mg, 1.92 mmol), $Pd(OAC)_2$ (7 mg, 0.032 mmol), P(*t*-Bu)$_3$ (13 mg, 0.064 mmol) and anhydrous toluene (5 mL) were introduced in a round bottom flask. The reaction mixture was stirred for 6 h at 110 °C under Ar atmosphere. The solution was filtered on celite, dried over $MgSO_4$, evaporated. The residue was purified by column chromatography on silica gel, eluting with cyclohexane/ethyl acetate (80:20) to afford **F3BnCz** as a yellow powder (300 mg, 62%). ^{1}H NMR (acetone-d6, 300 MHz) δ (ppm) 7.54 (d, J=2.1 Hz, 2H), 7.44 (s, 2H), 7.41-7,.9 (d, J=8.8 Hz, 2H), 7.12-7.09 (dd, J=8.8 Hz, 2.2 Hz, 2H), 6.85-6.82 (d, J=9.2 Hz, 8H), 6.79-6.75 (d, J=9.2 Hz, 8H), 3.70 (s, 12H). ^{13}C NMR (acetone-d6, 75 MHz) δ (ppm) 156.0, 154.2, 150.8, 143.6, 137.7, 132.0, 129.6, 126.1, 125.6, 125.1, 124.8, 116.6, 115.4, 112.9, 111.3, 54.7. ^{19} F NMR (acetone-d6, 282 MHz) δ (ppm) -134,4, -164,1. HRMS *m/z* calculated for $C_{46}H_{36}F_3N_3O_4$: 751.2652 ; found: 751.2632.


F
F
F
7
1
N
2
N
3
O
O
4
5
6
O
O
3
7
1
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5
6
7.54
7.54
7.44
7.41
7.39
7.12
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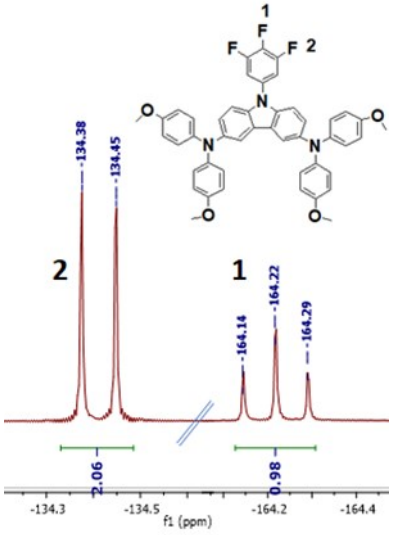
2.02
7.67
7.91
12.00
f1 (ppm)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F
2
N
O
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N
N
O
O
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2
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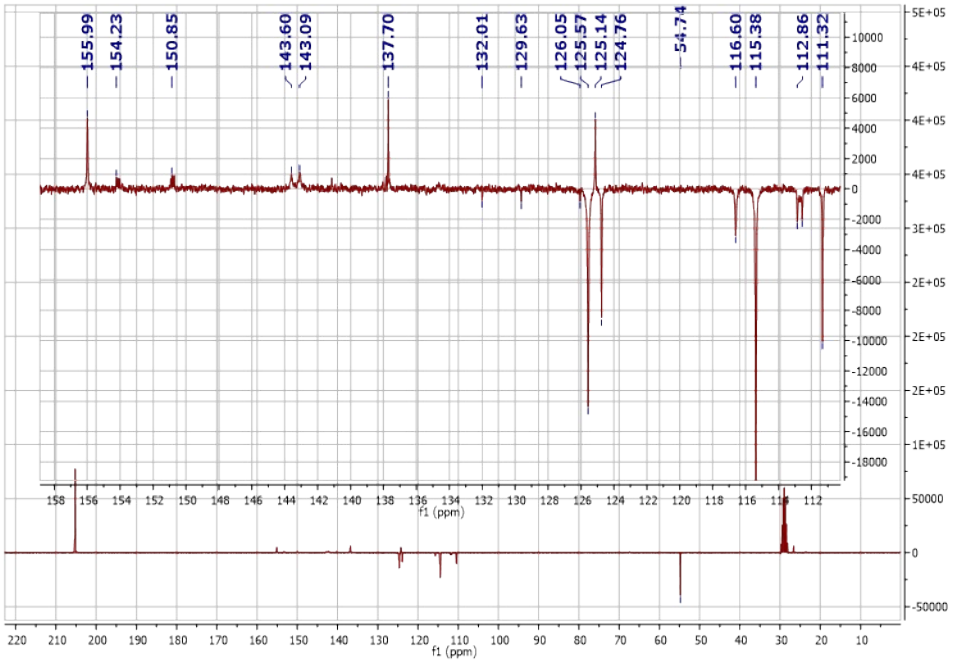
-164.4
f1 (ppm)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143.60
143.09
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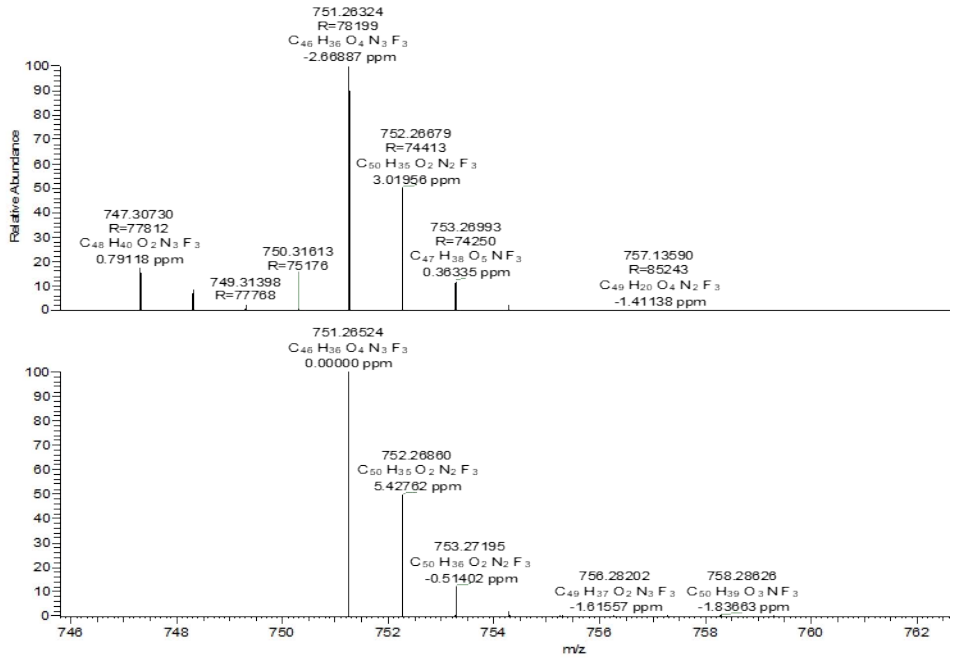
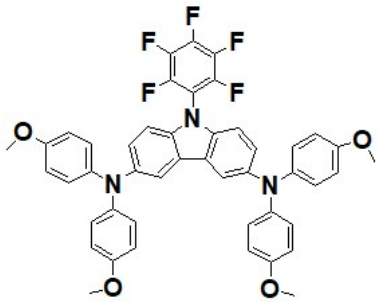
115.38
112.86
111.32
f1 (ppm)

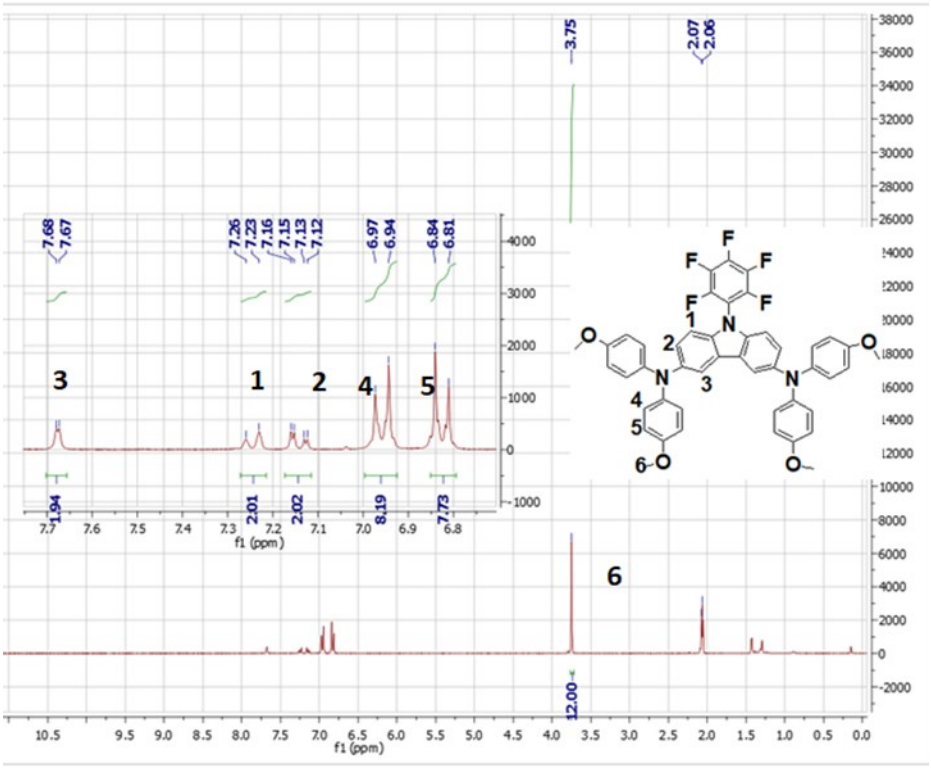


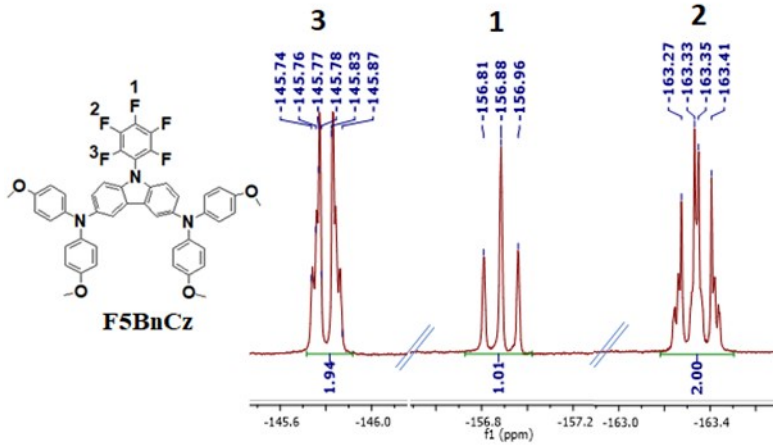


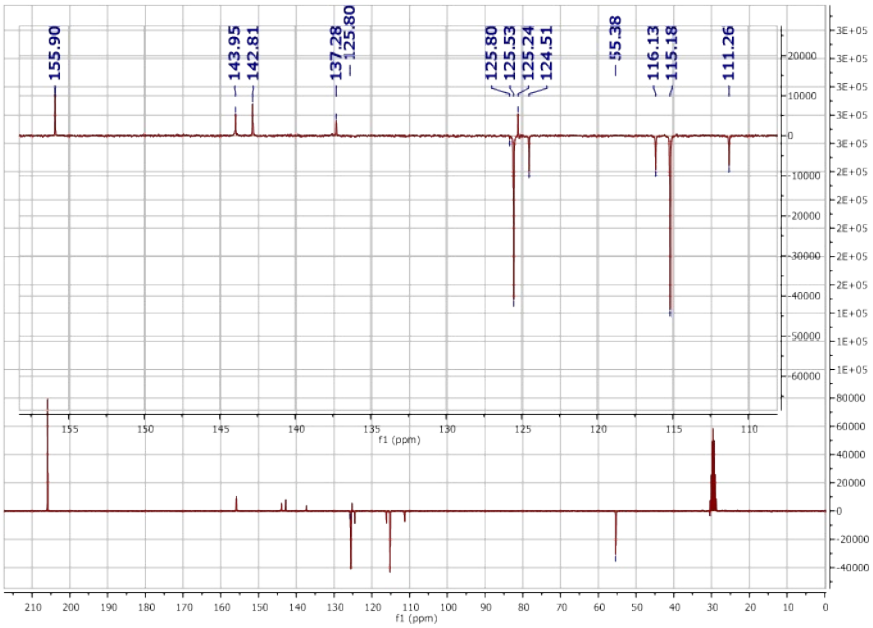
***N*³,*N*³,*N*⁶,*N*⁶-tetrakis(4-methoxyphenyl)-9-(hexafluorophenyl)-9H-carbazole-3,6-diamine (F5BnCz).**

*N*³,*N*³,*N*⁶,*N*⁶-tetrakis(4-methoxyphenyl)-9-*H*-carbazole-3,6-diamine **(3,6-CzDMPA)** (100 mg, 0.16 mmol) and NaH (10 mg, 0.225 mmol) were introduced in a Schlenck flask under Ar atmosphere. Anhydrous THF (3 mL) was added. The mixture was stirred for 30 min at room temperature, cooled to 0°C, and hexafluorobenzene (150 mg, 0.8 mmol) was added dropwise. The reaction mixture was stirred at 0°C for 6 h, distillated water was added (5 mL), the organic phase was extracted with CH_2Cl_2 (2x20 mL), washed with distillated water, then with brine, dried over $MgSO_4$, filtered, evaporated. The residue was purified by column chromatography on silica gel, eluting with cyclohexane/ethyl acetate (90:10) to afford **F5BnCz** as a yellow powder (71 mg, 56%). **^{1}H NMR (acetone-d6, 300 MHz) δ (ppm)** 7.67 (d, J=1.9 Hz, 2H), 7.25-7.22 (d, J=8.8 Hz, 2H), 7.15-7.12 (dd, J=8.8 Hz, 2.1 Hz, 2H), 6.97-6.94 (d, J=8.9 Hz, 8H), 6.83-6.80 (d, J=9.0 Hz, 8H), 3.74 (s, 12H). **^{13}C NMR (acetone-d6, 75 MHz) δ (ppm**) 155.9,

144.0, 142.8, 137.3, 125.8, 125.5, 125.2, 124.5, 116.1, 115.2, 111.3, 55.4. **^{19}F NMR (acétone-d6, 282 MHz) δ (ppm)** -145.7, -156.8, -163.2. **HRMS m/z** calculated for $C_{46}H_{34}F_5N_3O_4$: 787.2464 ; found : 787.2442.



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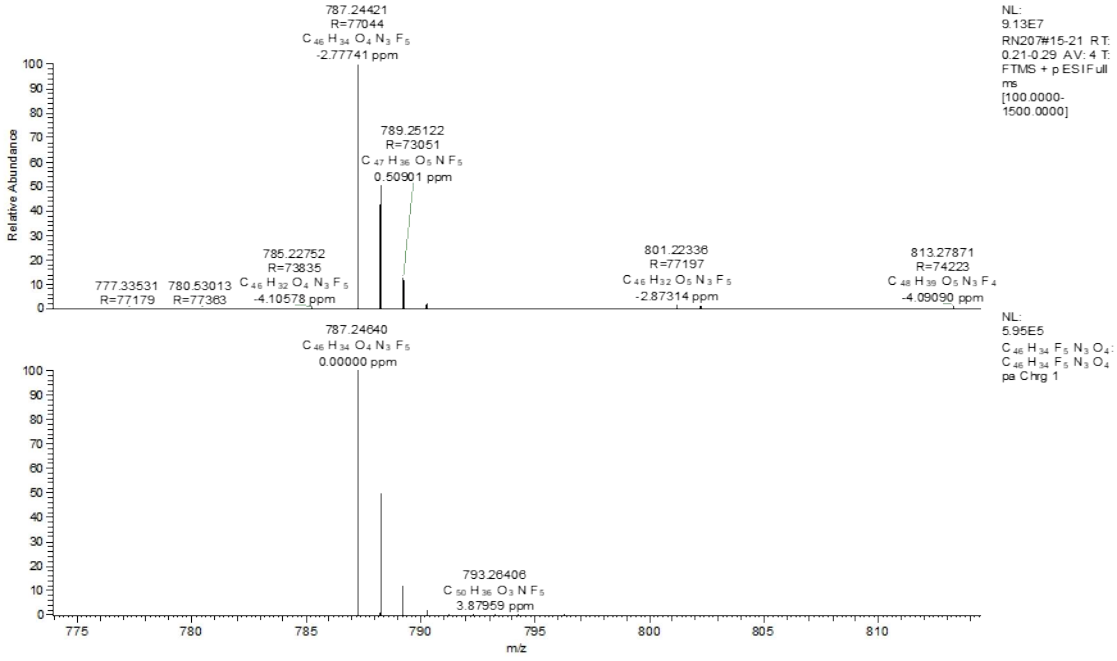
116.13
115.18
111.26
f1 (ppm)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789.25122
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785.22752
R=73835
C46 H32 O4 N3 F5
-4.10578 ppm
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R=77179
780.53013
R=77363
801.22336
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813.27871
R=74223
C48 H39 O5 N3 F4
-4.09090 ppm
Relative Abundance
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FTMS + p ESI Full
ms
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1500.0000]
787.24640
C46 H34 O4 N3 F5
0.00000 ppm
793.26406
C50 H36 O3 N F5
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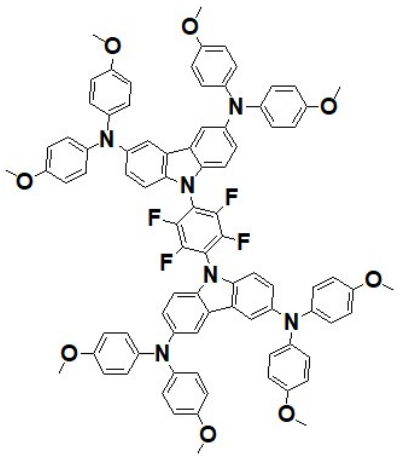
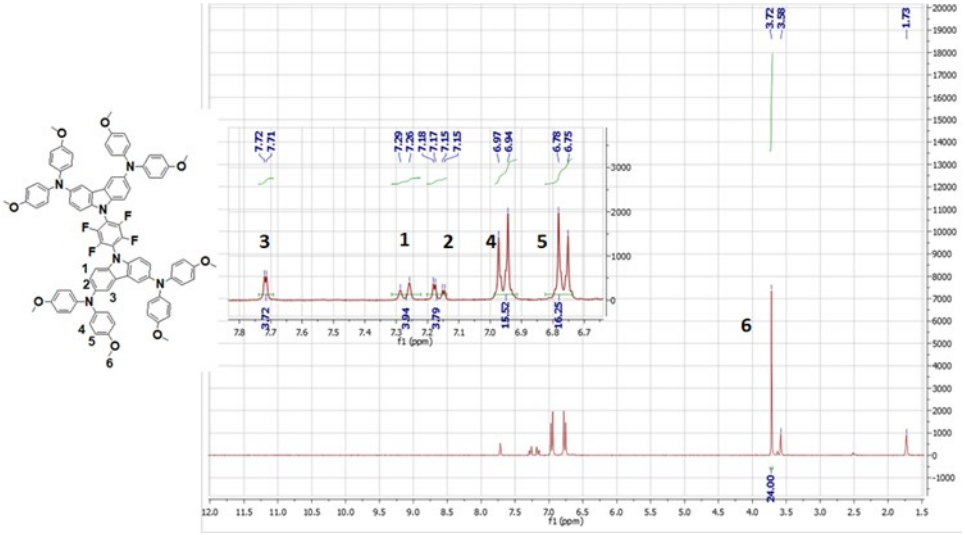
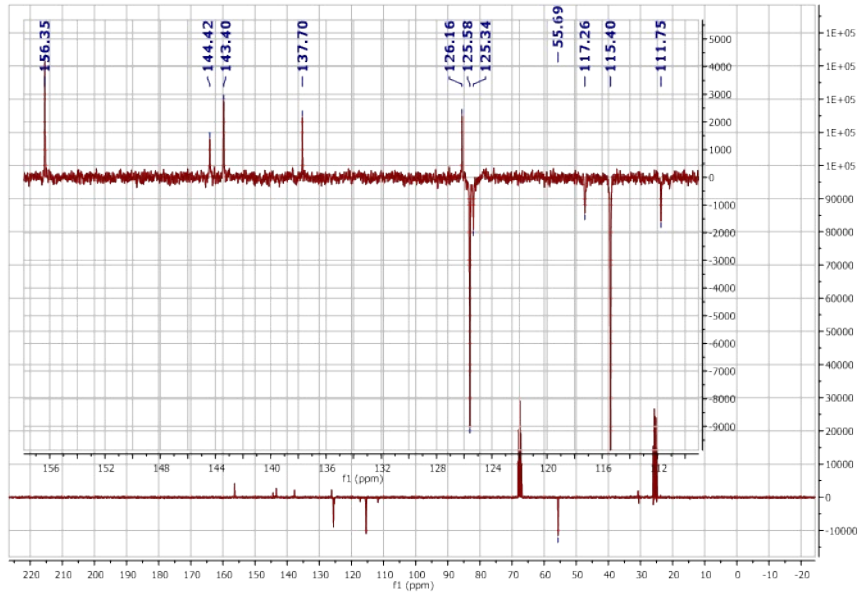
m/z
NL:
5.95E5
C46 H34 F5 N3 O4 :
C46 H34 F5 N3 O4
pa Chrg 1



N^3,N^3,N^6,N^6-tetrakis(4-methoxyphenyl)-9-(tetrafluorophenyl)-9H-carbazole-3,6-diamine **(F4BnCz2).**

N^3,N^3,N^6,N^6-tetrakis(4-methoxyphenyl)-9-*H*-carbazole-3,6-diamine **(3,6-CzDMPA)** (500 mg, 0.80 mmol) and NaH (50 mg, 1.20 mmol) were introduced in a Schlenck flask under Ar atmosphere. Anhydrous THF (5 mL) was added. The mixture was stirred for 30 min at room temperature. Hexafluorobenzene (50 mg, 0.27 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 6 h, distillated water was added (5 mL), the organic phase was extracted with CH_2Cl_2 (2x30 mL), washed with distillated water, then with brine, dried over $MgSO_4$, filtered, evaporated. The residue was purified by column chromatography on silica gel, eluting with cyclohexane/ethyl acetate (80:20) to afford **F4BnCz2** as a yellow powder (300 mg, 80%). **^{1}H NMR (THF-d8, 300 MHz) δ (ppm)** 7.72 (d, J=2.0 Hz, 4H), 7.29-7.26 (d, J=8.7 Hz, 4H), 7.18-7.15 (dd, J=8.8 Hz, 2.0 Hz, 4H), 6.97-6.94 (d, J=9.0 Hz, 16H), 6.78-6.75 (d, J=9.0 Hz, 16H), 3.72 (s, 24H). **^{13}C NMR (THF-d8, 75 MHz) δ (ppm)** 156.4, 144.4, 143.4, 137.7, 126.2, 125.6, 125.3, 117.3, 115.4, 111.8, 55.7. **^{19} F NMR (acétone-d6, 282 MHz) δ (ppm) -**146.0. **HRMS m/z** calculated for $C_{86}H_{68}F_4N_6O_8$: 1388.5 ; found: (M+1) 1389.5.

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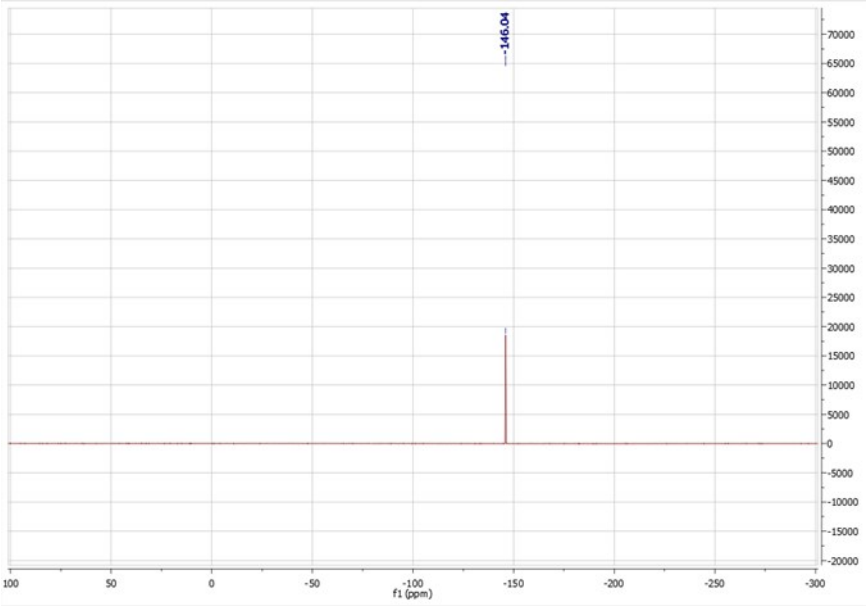
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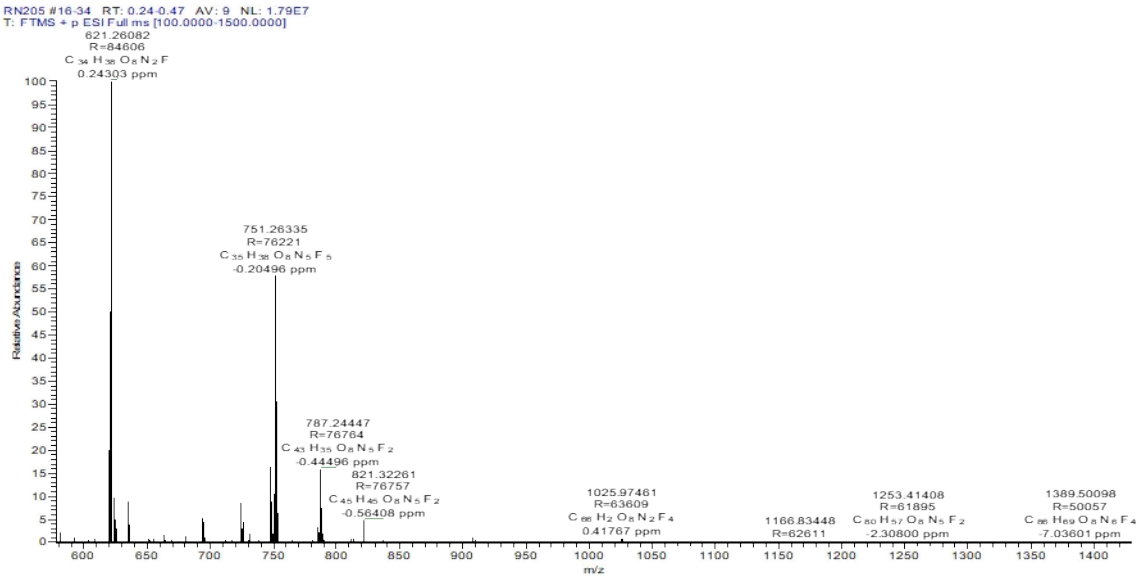
f1 (ppm)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787.24447
R=76764
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-0.44496 ppm
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R=76757
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Relative Abundance
m/z

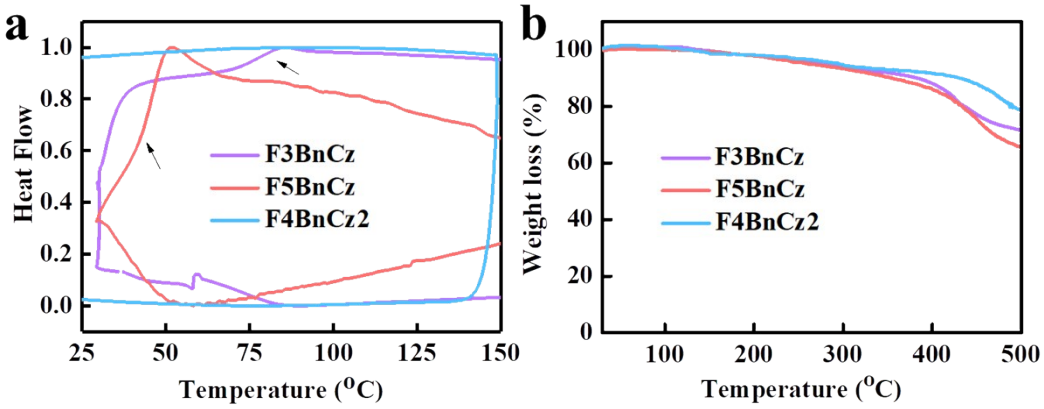

Figure S1 a) Differential scanning calorimetry (DSC) b) therrmogravimetric analysis (TGA) of three molecules.

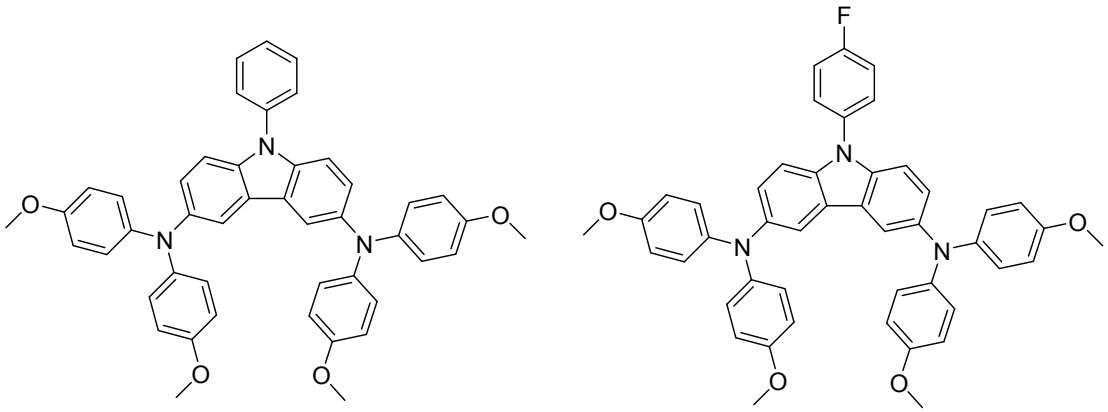

Figure S2 Chemical structures of **CzP** and **CzPF**.

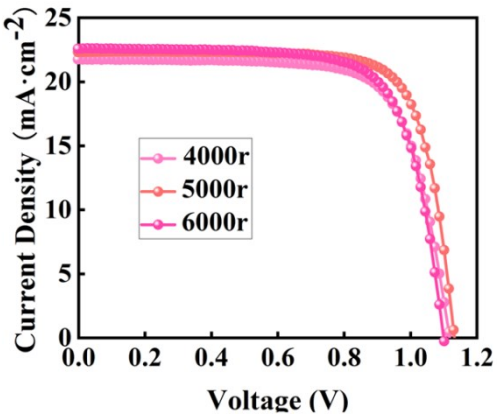

Figure S3 Current density-voltage (*J-V*) curves of the F5BnCz-based devices under different spin speed.

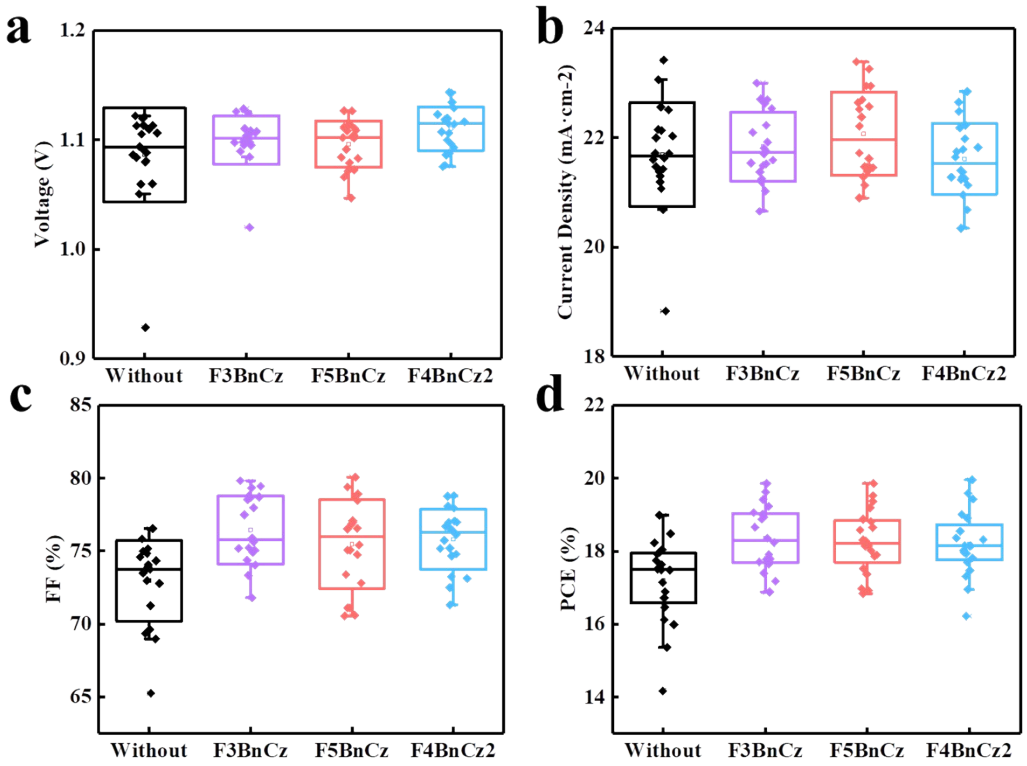

Figure S4 a) Open-circuit voltage, b) short-circuit current density, c) *FF* and d) *PCE* distributions for the corresponding device

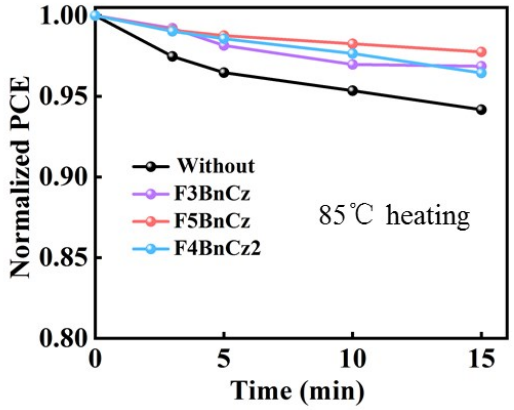

Figure S5 Thermal stability of the PSCs with and without interfacial layers under 85℃.

Table S1 Photovoltaic parameters of F5BnCz-based devices under different spin speed.

	V_{OC} [V]	J_{SC} [mA/cm^2]	*FF* [%]	*PCE* [%]
4000r	1.12	21.75	72.91	17.71
5000r	1.13	22.33	76.22	19.24
6000r	1.10	22.60	72.88	18.09

Table S2 The time constant and amplitude extracted from fitting the TRPL data with biexponential decay equation ($I = A_1 \exp\left[\frac{-(t-t_0)}{\tau_1}\right] + A_2 \exp\left[\frac{-(t-t_0)}{\tau_2}\right]$) for devices.

	A_1	τ_1 (ns)	A_2	τ_2 (ns)
Perovskite	1120	24.71	1705	59.97
Spiro-OMeTAD	1150	21.53	2404	51.02
w F3BnCz	2104	4.39	909	12.70
w F5BnCz	609	12.86	2188	47.50
w F4BnCz2	765	18.87	1635	49.95