Electronic Supplementary Material (ESI) for Chemical Science.

A Structure-Property Study of Fluoranthene-cored Hole Transporting Materials Enables 19.3% Efficiency Dopant-free Perovskite Solar Cells

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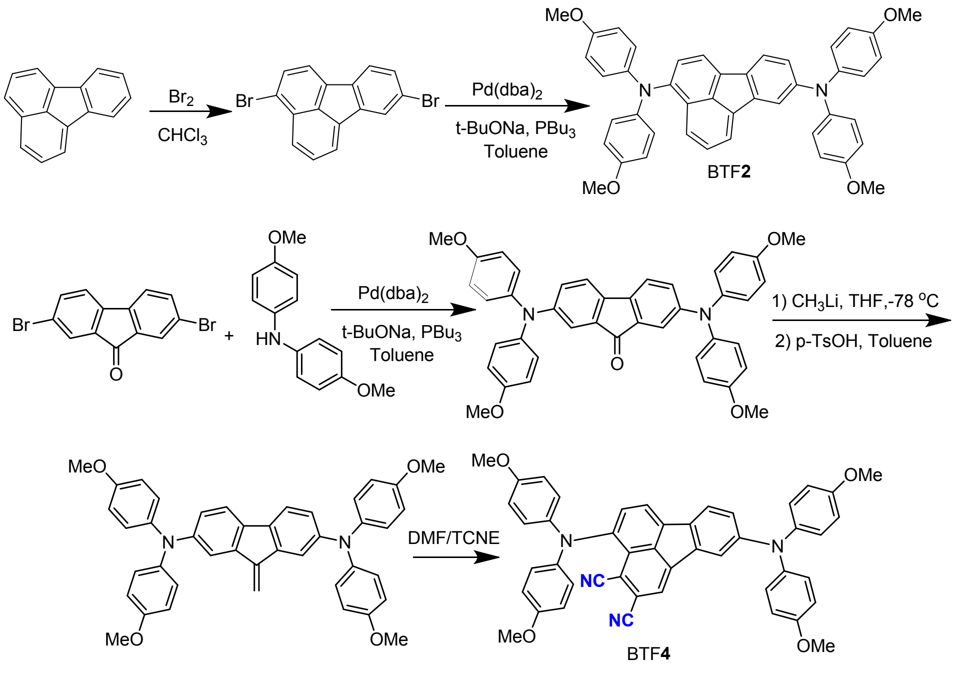
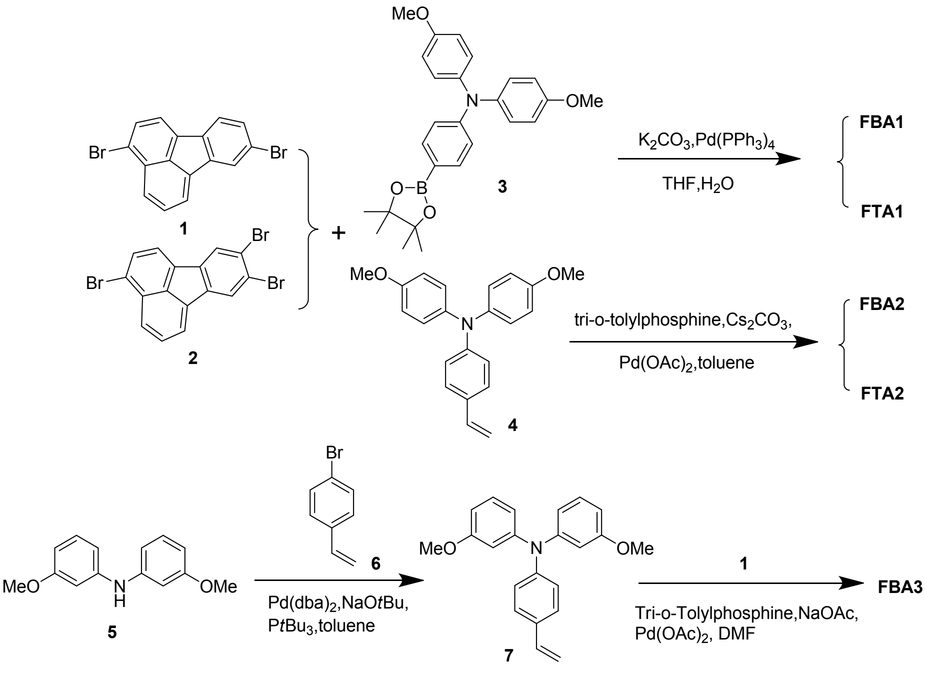


Scheme S1. Synthetic route of **BTF2** and **BTF4**.



Scheme S2. Synthetic route of fluoranthene-based HTMs.

Instrumentations.

^{1}H NMR and ^{13}C NMR spectra were measured using a Bruker 400 or 600 MHz instrument spectrometer. High-resolution mass spectrometry (MS) was performed by using Bruker Daltonics instrument, SolariX 7.0T. MALDI MS analysis was performed on an AB SCIEX MALDI TOF/TOF™ 5800 system (Applied Biosystems, Foster City, CA, USA). Cyclic voltammetry was measured on a CHI6001 electrochemical analyzer (CH Instruments, Inc., China) using a conventional three-electrode cell with Pt metal as the working electrode, Pt gauze as the counter-electrode, and Ag/Ag$^+$ as the reference electrode at a scan rate of 50 mV/s. Thermal transition was measured on a NETZSCH STA 449 F3 Jupiter with a heating rate of 10 °C min^{-1}. UV−vis−IR absorption spectra were collected using a Perkin Elmer UV-VIS-NIR spectrophotometer Lambda 750 S. The PL spectra were collected on a SHIMADZU RF-5301PC Spectrofluorophotometer. AFM was measured by using SHIMADZU SPM-9700SPM-9700.

Materials.

Toluene, 1,4-dioxane and tetrahydrofuran (THF) were dried and distilled from sodium under an atmosphere of dry nitrogen. Most of reagents were purchased from Adamas (Titan Scientific, Shanghai), except $Pd(OAc)_2$ (Fluorochem), $Pd(dba)_2$ (Frontier). Compounds **3**-**5** and **7** were synthesized as reported,[1-3] while their synthetic costs were also determined to 3.3 \$/g, 1.0 \$/g, 0.9 \$/g and 3.9 \$/g, respectively.

For device fabrication, all materials and solvents were commercially available and directly used without further purification, including MAI (*p*-OLED, ≥99.5 %), PbI_2 (*p*-OLED, >99.99 %), $PbCl_2$ (*p*-OLED, >99.99 %), C_{60} (*p*-OLED, >99.5%), MoO_3 (Sigma-Aldrich, 99.97 %), Spiro-OMeTAD (*p*-OLED, ≥99.5 %), Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) (Heraeus, Clevios PVP Al 4083), *N,N*-dimethylformamide (DMF) (Sigma-Aldrich, 99.8 %), Dimethyl sulfoxide (DMSO) (Sigma-Aldrich, 99.8 %) and chlorobenzene (CB) (Sigma-Aldrich, 99.8 %).

Device Fabrication: Patterned ITO substrates were cleaned in an ultrasonic bath in detergent, deionized water, acetone, isopropanol sequentially, following with a plasma for 3 min. Under high vacuum, 20 nm thick of C_{60} film was deposited onto these ITO substrates as the electron-transporting layer (ETL) through a thermal evaporation method with a rate of ~1 nm/min. Then in the N_2-filled glovebox, a perovskite precursor solution containing 1.26 M PbI_2, 0.14 M $PbCl_2$ and 1.4 M MAI in the mixed DMF/DMSO solution (V/V, 4:1) was spin-coated onto the above substrates using the two-step processing program at 400 and 5000 rpm for 3 and 30 s, respectively. 200 μL of CB was dropped onto the spinning substrate at 10 s after begining during the second step. Next, the as-spun perovskite films were annealed on a hot plate at 60 °C for 1 min and then 85 °C for 25 min to drive off solvent, leading to the perovskite phase. After that, fluoranthene-cored molecules were deposited ontop the perovskites by spin-coating their CB solutions at 4000 rpm for 30 s as hole transporting layers (HTLs) in the absence of dopants. The solution concentration was controlled at 6~12 mg/mL to optimize the film thickness. Spiro-OMeTAD precursor solution in CB (72.5 mg Spiro-OMeTAD, 28.5 μL *t*BP and 17.5 μL Li-TSFI stock solution (520 mg mL^{-1} in acetonitrile) was spin-coated on the perovskite layer (5000 rpm, 60 s) to deposit the HTM layer. Afterwards, the HTM layer undergoes oxidation for 15 h in an air atmosphere. Finally, a 10 nm thick of MoO_3 layer and sequentially a ~100 nm thick of Ag counter electrode were thermally evaporated to complete the device fabrication. The active area of our device is controlled at 0.04 cm^2.

Mobility Measurements: Hole-only devices were fabricated with a typical structure ITO/PEDOT:PSS/HTMs/MoO_3(10 nm)/Ag(100 nm). The dark *J–V* characteristics were characterized in the N_2-filled glovebox. Mobility data is extracted by fitting the current density-voltage curves based on space charge limited current (SCLC).

Device Analysis: The cross-sectional scanning electron microscope (SEM) images were collected by FE-SEM images (JSM-7800F). Steady-state photoluminance (PL) spectra were recorded on the Fluorolog®-3 fluorescence spectrometer (Horiba), while time-resolved PL decay curves were collected by a single photon counting spectrometer from Horiba Instruments (Fluorolog®-3) with a Picosecond Pulsed UV-LASTER (LASTER375) as the excitation source. The current–voltage (*J–V*) curves of PVSCs were measured under 100 mW cm^{-2} (AM 1.5 G) simulated sunlight using Keithley 2400 in conjunction with a Newport solar simulator (94043A). The external quantum efficiency (EQE) was calculated from the photocurrent measurement under monochromatic illuminations at different wavelengths, using a 150 W xenon lamp and a monochromator.

S2. Synthetic Details and Characterization Data

Synthesis of FBA1

A mixture of 3,8-dibromofluoranthene (**1**, 0.27 g, 0.75 mmol), 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**3**, 0.65 g, 1.50 mmol), K_2CO_3 (0.30 g, 2.25 mmol) and $Pd(PPh_3)_4$ (0.05 g, 0.05 mmol) in dry THF (10 mL) and degassed water (5 mL) was heated to 70 °C under nitrogen for 24 h. After cooling down to room temperature, the mixture was extracted with dichloromethane (DCM). The organic layer was collected, washed with water and dried with anhydrous Na_2SO_4. After concentration using a rotary evaporator, the crude product was purified by column chromatography on the silica gel using petroleum ether/DCM (V/V:1/2) as the eluent to obtain **FBA1** as a yellow solid (0.27 g, 44.6%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (s, 1H, ArH), 8.04 (d, *J* = 8.4 Hz, 1H, ArH), 8.02-7.97 (m, 1H, ArH), 7.94 (d, *J* = 7.2 Hz, 1H, ArH), 7.91 (d, *J* = 8.0 Hz, 1H, ArH), 7.61-7.65 (m, 1H, ArH), 7.59 (d, *J* = 7.3 Hz, 2H, ArH), 7.55 (d, *J* = 7.0 Hz, 2H, ArH), 7.43 (d, *J* = 8.1 Hz, 2H, ArH), 7.21-6.97 (m, 12H, ArH), 6.89-6.85 (m, 8H, ArH), 3.82 (s, 12H, -OCH$_3$). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.03, 155.90, 148.20, 140.86, 140.15, 140.10, 140.01, 137.50, 137.12, 135.55, 133.29, 131.59, 130.90, 130.86, 128.82, 128.49, 128.33, 127.81, 127.56, 126.84, 126.59, 125.95, 125.84, 121.52, 120.91, 120.04, 119.88, 119.77, 119.64, 114.80, 114.75, 55.53. HRMS (APCI): $(M+H)^+$ = 809.3366 (calcd for $C_{56}H_{45}N_2O_4^+$, 809.3379)

Synthesis of FTA1

A mixture of 3, 8, 9-tribromofluoranthene (**2**, 0.22 g, 0.50 mmol), compound **3** (1.08 g, 2.50 mmol), K_2CO_3 (0.21 g, 1.50 mmol) and $Pd(PPh_3)_4$ (0.05 g, 0.05 mmol) in dry THF (10 mL) and degassed water (5 mL) was heated to 70 ℃ under nitrogen for 24 h. After cooling down to room temperature, the mixture was extracted with DCM. The organic layer was collected, washed with water and dried with anhydrous Na_2SO_4. After concentration using a rotary evaporator, the crude product was purified by column chromatography on the silica gel using petroleum ether/DCM (V/V:1/3) as the eluent to obtain **FTA1** as a yellow solid (0.25 g, 44.8%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.4 Hz, 1H, ArH), 7.97-7.93 (m, 4H, ArH), 7.63 (t, *J* = 7.6 Hz, 1H, ArH), 7.60 (d, *J* = 7.2 Hz, 1H, ArH), 7.44 (d, *J* = 8.2 Hz, 2H, ArH), 7.21-7.01 (m, 18H, ArH), 6.89-6.83 (m, 16H, ArH), 3.82 (s, 6H, -OCH$_3$), 3.80 (s, 12H, -OCH$_3$). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.03, 155.70, 148.2, 141.11, 140.87, 140.11, 139.84, 139.59, 138.26, 137.95, 137.05, 135.63, 134.58, 133.54, 131.61, 130.86, 130.60, 128.50, 128.32, 127.89, 126.84, 126.37, 125.73, 123.36, 123.21, 120.26, 120.09, 120.05, 119.82, 114.80, 114.67, 55.53, 55.51. HRMS (APCI): $(M+H)^+$ = 1112.4612 (calcd for $C_{76}H_{62}N_3O_6^+$, 1112.4639).

Synthesis of FBA2

A mixture of compound **1** (0.29 g, 0.80 mmol), compound **4** (0.79 g, 2.38 mmol), tri-*o*-tolylphoshine (0.02 g, 0.06 mmol), Cs_2CO_3 (1.60 g, 4.80 mmol) and $Pd(OAc)_2$ (6.7 mg, 0.03 mmol) in dry toluene (10 mL) was heated to 120 ℃ under nitrogen for 48 h. After cooling down to room temperature, the mixture was extracted with DCM. The organic layer was collected, washed with water and dried with anhydrous Na_2SO_4. After concentration using a rotary evaporator, the crude product was purified by column chromatography on the silica gel using petroleum ether/DCM (V/V:1/3) as the eluent to obtain **FBA2** as a red solid (0.23 g, 33.9%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 8.5 Hz, 1H, ArH), 8.04 (s, 1H, ArH), 7.99 (d, *J* = 6.9 Hz, 1H, ArH), 7.95-7.89 (m, 2H, ArH), 7.83 (d, *J* = 7.8 Hz, 1H, ArH), 7.75 (d, *J* = 16.1 Hz, 1H, -CH=CH-), 7.69-7.65 (m, 1H, ArH), 7.46 (m, 3H, ArH and -CH=CH-), 7.38 (d, *J* = 8.4 Hz, 2H, ArH), 7.23-7.01 (m, 11H, ArH and -CH=CH-), 7.00-6.81 (m, 12H, ArH), 3.81 (br, s, 12H,-OCH_3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.06, 155.97, 148.63, 148.32, 140.77, 140.66, 139.99, 138.03, 137.09, 137.06, 135.78, 135.26, 133.34, 131.16, 129.74, 128.42, 128.03, 127.71, 127.52, 127.26, 126.75, 126.67, 126.43, 125.95, 124.22, 123.51, 121.63, 121.42, 120.50, 120.38, 120.23, 120.03, 119.00, 114.77, 114.74, 55.52. HRMS (APCI): $(M+H)^+$ = 861.3678 (calcd for $C_{56}H_{49}N_2O_4^+$, 861.3692)

Synthesis of FTA2

A mixture of compound **2** (0.33 g, 0.75 mmol), compound **4** (0.99 g, 3.0 mmol), tri-*o*-tolylphoshine (0.03 g, 0.11 mmol), Cs_2CO_3 (1.5 g, 4.5 mmol) and $Pd(OAc)_2$ (13 mg, 0.06 mmol) in dry toluene (10 mL) was heated to 120 ℃ under nitrogen for 48 h. After cooling down to room temperature, the mixture was extracted with DCM. The organic layer was collected, washed with water and dried with anhydrous Na_2SO_4. After concentration using a rotary evaporator, the crude product was purified by column chromatography on the silica gel using petroleum ether/DCM (V/V:1/4) as the eluent for three times to obtain **FTA2** as a red solid (0.14 g, 15.7%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.5 Hz, 1H, ArH), 8.07 (d, *J* = 7.4 Hz, 1H, ArH), 7.96 (d, *J* = 6.9 Hz, 1H, ArH), 7.94-7.89 (m, 2H, ArH), 7.79-7.61 (m, 3H, ArH,), 7.55-7.50 (m, 1H, ArH), 7.47-7.38 (m, 7H, ArH and -CH=CH-), 7.22 (d, *J* = 15.6 Hz, 1H, -CH=CH-), 7.15-7.12 (m, 1H, ArH), 7.09 (m, 12H, ArH), 6.95 (t, *J* = 8.4 Hz, 6H, ArH), 6.91-6.88 (m, 1H, -CH=CH-), 6.87-6.82 (m, 12H, ArH,), 3.82 (s, 6H, $-OCH_3$), 3.81 (s, 12H, $-OCH_3$). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.05, 155.97, 148.60, 148.36, 140.75, 140.67, 138.47, 138.19, 137.16, 135.85, 135.63, 135.31, 135.24, 133.82, 131.09, 130.88, 130.24, 130.15, 130.01, 129.77, 129.04, 128.81, 128.46, 127.78, 124.47, 124.18, 123.18, 121.66, 120.49, 120.39, 120.09, 119.72, 119.13, 118.95, 114.76, 114.74, 55.51. MALDI-TOF: (M^+) = 1189.6582 (calcd for $C_{82}H_{67}N_3O_6^+$, 1189.5030).

Synthesis of 7

A mixture of bis(3-methoxyphenyl)amine (**5**, 2.30 g, 10.0 mmol), 1-bromo-4-vinylbenzene (**6**, 1.83 g, 10.0 mmol), $Pd(dba)_2$ (0.12 g, 0.2 mmol), NaO*t*Bu (2.40 g, 25.0 mmol) and P*t*Bu$_3$ (0.75 mL, 0.3 mmol) in dry toluene (10 mL) was heated to reflux under nitrogen for 24 h. After cooling down to room temperature, the mixture was extracted with DCM. The organic layer was collected, washed with water and dried with anhydrous Na_2SO_4. After concentration using a rotary evaporator, the crude product was purified by column chromatography on the silica gel using petroleum ether/DCM (V/V:3/1) as the eluent to obtain **7** as a white solid (2.40 g, 72.7%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.6 Hz, 2H, ArH), 7.15 (t, *J* = 8.1 Hz, 2H, ArH), 7.04 (d, *J* = 8.6 Hz, 2H, ArH), 6.70-6.62 (m, 5H, ArH and $-CH=CH_2$), 6.58 (dd, *J* = 8.2, 2.5 Hz, 2H, ArH), 5.64 (d, *J* = 17.6 Hz, 1H, CH_2=CH-), 5.16 (d, *J* = 10.9 Hz, 1H, CH_2=CH-), 3.72 (s, 6H, -OMe). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.46, 148.73, 147.22, 136.25, 132.16, 129.81, 127.03, 124.09, 116.91, 112.28, 110.20, 108.48, 55.26.

Synthesis of FBA3

A mixture of compound **1** (0.29 g, 0.80 mmol), compound **7** (0.79 g, 2.40 mmol), tri-*o*-tolylphoshine (0.02 g, 0.06 mmol), NaOAc (0.13 g, 1.60 mmol) and $Pd(OAc)_2$ (7.2 mg, 0.03 mmol) in dry DMF (8 mL) was heated to 140 ℃ under nitrogen for 48 h. After the mixture was cooled to room temperature, it was poured into water and extracted with DCM, the organic solution was dried with Na_2SO_4, after filtration, the resulting solution was concentrated by a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/DCM (V/V:1:3) as the eluent to obtain **FBA3** as an orange solid (0.30 g, 43.6%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.4 Hz, 1H, ArH), 8.06 (d, *J* = 1.5 Hz, 1H, ArH), 8.01 (d, *J* = 6.8 Hz, 1H, ArH), 7.91 (s, 2H, ArH), 7.85 (d, *J* = 7.9 Hz, 1H, ArH), 7.82 (d, *J* = 16.1 Hz, 1H, -CH=CH-), 7.69 (dd, *J* = 8.4, 6.9 Hz, 1H, ArH), 7.52-7.49 (m, 3H, ArH, -CH=CH-), 7.45 (d, *J* = 8.6 Hz, 2H, ArH), 7.26 (d, *J* = 15.6 Hz, 1H, -CH=CH-),7.18 (m, 6H, ArH, -CH=CH-), 7.15-7.08 (m, 4H, ArH), 6.75-6.70 (m, 4H, ArH), 6.69 (dt, *J* = 7.0, 2.3 Hz, 4H, ArH), 6.61 (ddd, *J* = 8.8, 7.0, 2.5 Hz, 4H, ArH), 3.75 (s, 6H, $-OCH_3$), 3.74 (s, 6H, $-OCH_3$). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.52, 160.50, 148.68, 148.61, 147.42, 147.08, 140.04, 138.23, 137.04, 136.93, 135.99, 135.09, 133.33, 131.90, 130.99, 129.91, 129.88, 128.44, 127.84, 127.61, 127.53, 127.36, 126.13, 124.46, 124.08, 123.95, 123.54, 122.80, 121.50, 120.28, 120.12, 119.13, 117.13, 117.05, 110.44, 110.34, 108.73, 108.63, 55.30. HRMS (APCI): $(M+H)^+$ = 861.3679 (calcd for $C_{56}H_{49}N_2O_4^+$, 861.3692)

Table S1. Synthetic cost for the synthesis of **FBA1**.

Chemical	**Weight reagent (g/g)**	**Weight solvent (g/g)**	**Weight workup (g/g)**	**Price of Chemical ($/Kg)**	**Chemical cost $/g product)**	**Cost per step ($/step)**
1	1.00			1230	1.23	
3	2.40			3348	8.04	
K_2CO_3 (adamas)	1.15			5.81	0.01	
$Pd(PPh_3)_4$ (adamas)	0.19			6987	1.33	
THF (adamas)		33		32.27	1.06	
Na_2SO_4 (general source)			1.0	3.29	0.00	
DCM (general source)			300.00	0.91	0.27	
Silica gel (general source)			50.00	8.73	0.44	
Petroleum ether (general source)			100.00	1.74	0.17	
						12.55

Table S2. Synthetic cost for the synthesis of **FBA2**.

Chemical	Weight reagent (g/g)	Weight solvent (g/g)	Weight workup (g/g)	Price of Chemical ($/Kg)	Chemical cost $/g product)	Cost per step ($/step)
1	1.23			1230	1.51	
4	3.39			10000	33.9	
Cs_2CO_3 (adamas)	6.84			445	3.04	
$Pd(OAc)_2$ (adamas)	0.029			26200	0.76	
Tri-o-Tolylphosphine	0.078			1001	0.08	
Toluene (general source)		37.18		6.40	0.24	
Na_2SO_4 (general source)			1.0	3.29	0.00	
DCM (general source)			400.00	0.91	0.36	
Silica gel (general source)			50.00	8.73	0.44	
Petroleum ether (general source)			100.00	1.74	0.17	
						40.50

Table S3. Synthetic cost for the synthesis of **FBA3**.

Chemical	Weight reagent (g/g)	Weight solvent (g/g)	Weight workup (g/g)	Price of Chemical ($/Kg)	Chemical cost $/g product)	Cost per step ($/step)
1	0.96			1230	1.18	
7	2.64			3908	10.36	
NaOAc (adamas)	0.44			38.7	0.00	
$Pd(OAc)_2$ (adamas)	0.024			26200	0.63	
Tri-o-Tolylphosphine	0.065			1001	0.07	
DMF (general source)		27		3.66	0.10	
Na_2SO_4 (general source)			1.0	3.29	0.00	
DCM (general source)			1400.00	0.91	1.27	
Silica gel (general source)			50.00	8.73	0.44	
Petroleum ether (general source)			400.00	1.74	0.70	
						14.75

Table S4. Synthetic cost for the synthesis of **FTA1**.

Chemical	**Weight reagent (g/g)**	**Weight solvent (g/g)**	**Weight workup (g/g)**	**Price of Chemical ($/Kg)**	**Chemical cost $/g product)**	**Cost per step ($/step)**
2	0.88			1009	0.89	
3	4.32			3348	14.46	
K_2CO_3 (adamas)	0.83			5.81	0.00	
$Pd(PPh_3)_4$ (adamas)	0.21			6987	1.47	
THF(adamas)		35.6		32.27	1.15	
Na_2SO_4 (general source)			1.0	3.29	0.00	
DCM (general source)			500.00	0.91	0.46	
Silica gel (general source)			50.00	8.73	0.44	
Petroleum ether (general source)			300.00	1.74	0.52	
						19.39

Table S5. Synthetic cost for the synthesis of **FTA2**.

Chemical	**Weight reagent (g/g)**	**Weight solvent (g/g)**	**Weight workup (g/g)**	**Price of Chemical ($/Kg)**	**Chemical cost $/g product)**	**Cost per step ($/step)**
2	3.14			1009	3.16	
4	7.09			10000	70.9	
Cs_2CO_3 (adamas)	10.7			445	4.76	
Pd(OAc)2 (adamas)	0.09			26200	2.36	
Tri-o-Tolylphosphine	0.24			1001	0.24	
Toluene (general source)		93.2		6.40	0.60	
Na_2SO_4 (general source)			8.0	3.29	0.00	
DCM (general source)			2400.00	0.91	2.18	
Silica gel (general source)			150	8.73	1.30	
Petroleum ether (general source)			800.00	1.74	1.39	
						86.1

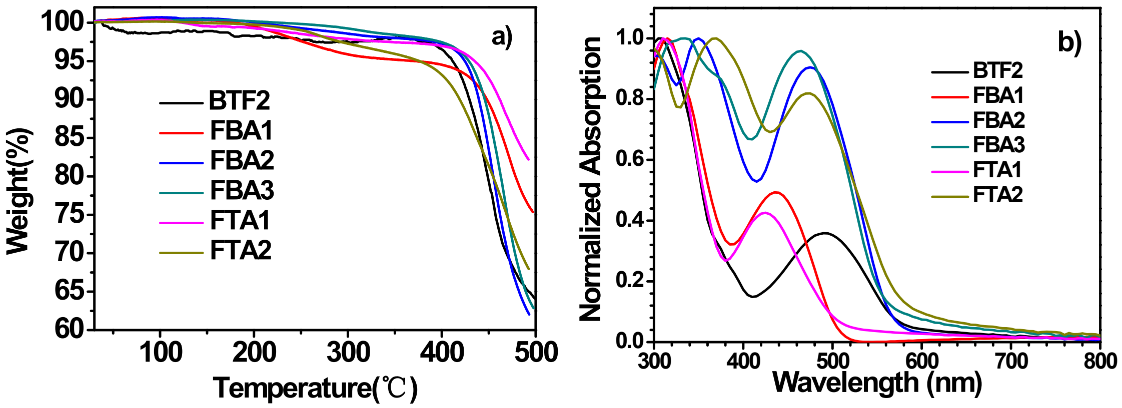


Figure S1. TGA curves (a) and film absorption spectra (b) of fluoranthene-cored HTMs.

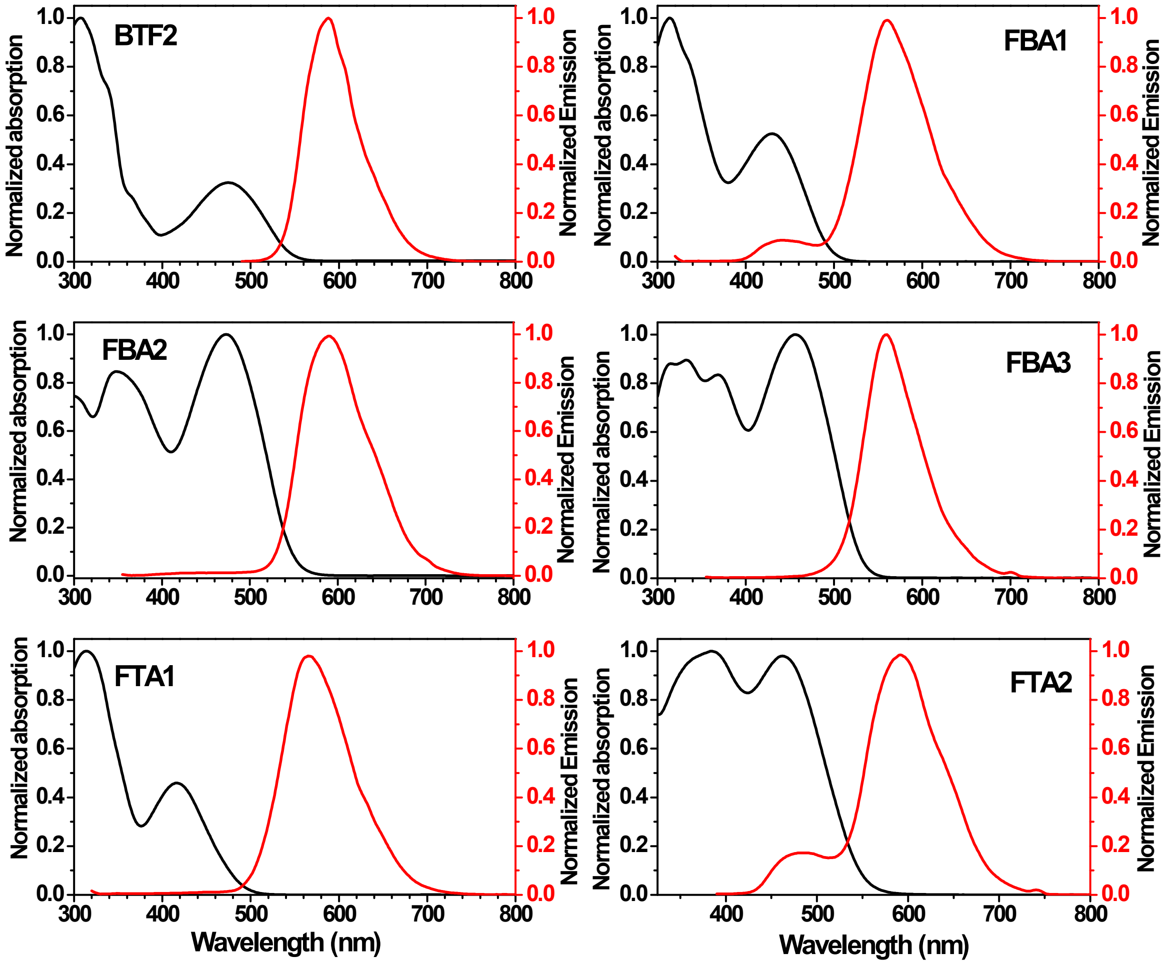


Figure S2. The absorption spectra (black) of emission spectra (red) of fluoranthene-cored HTMs in diluted DCM solutions.

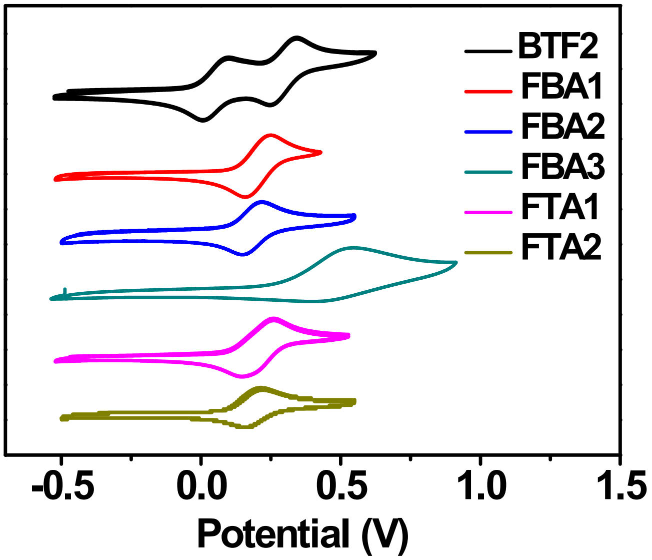


Figure S3. CV curves of fluoranthene-cored HTMs measured in DCM solutions.

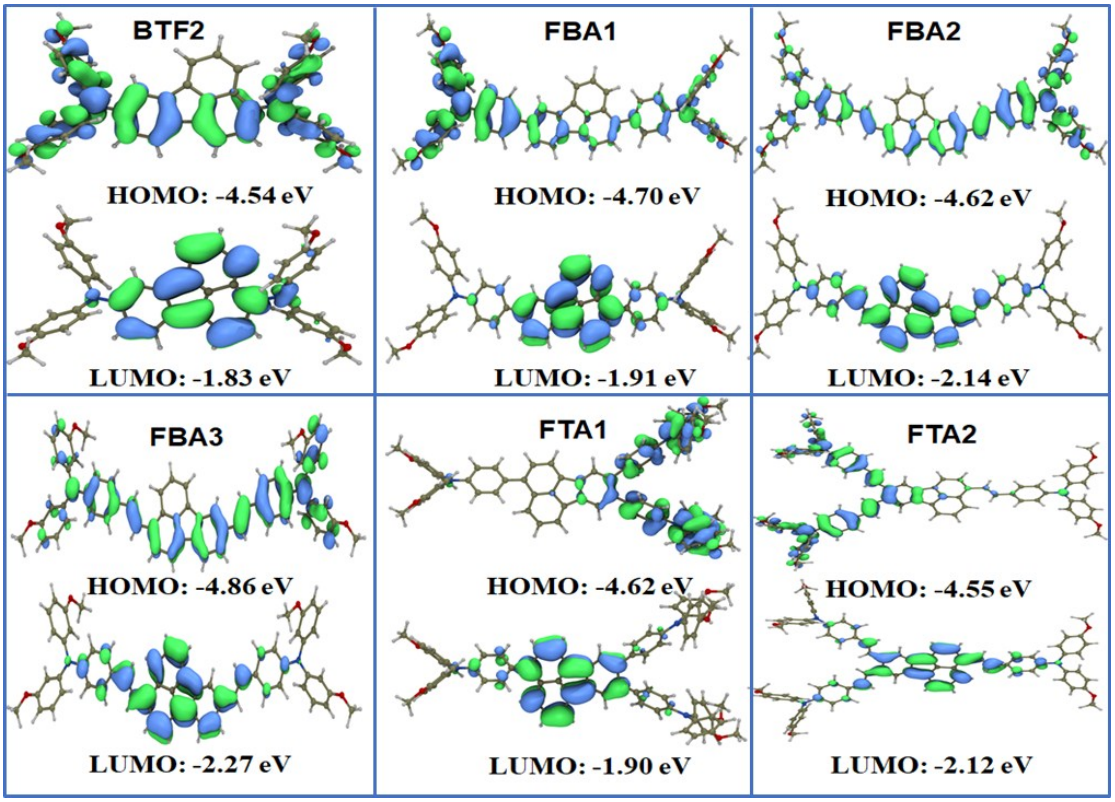


Figure S4. DFT-calculated HOMOs and LUMOs of fluoranthene-cored HTMs.

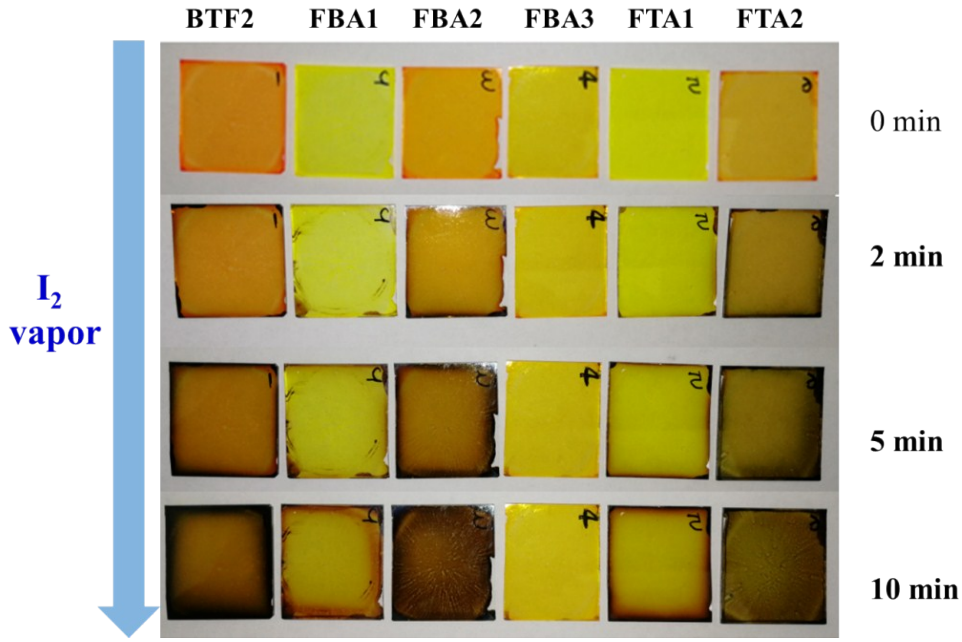


Figure S5. Color variation of fluoranthene-cored HTM films on a glass substrate before and after I_2 vapor treatment with different times.

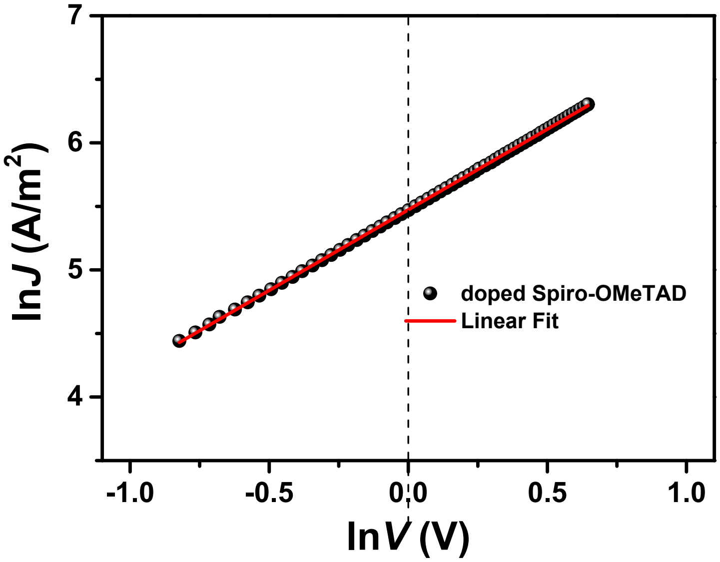
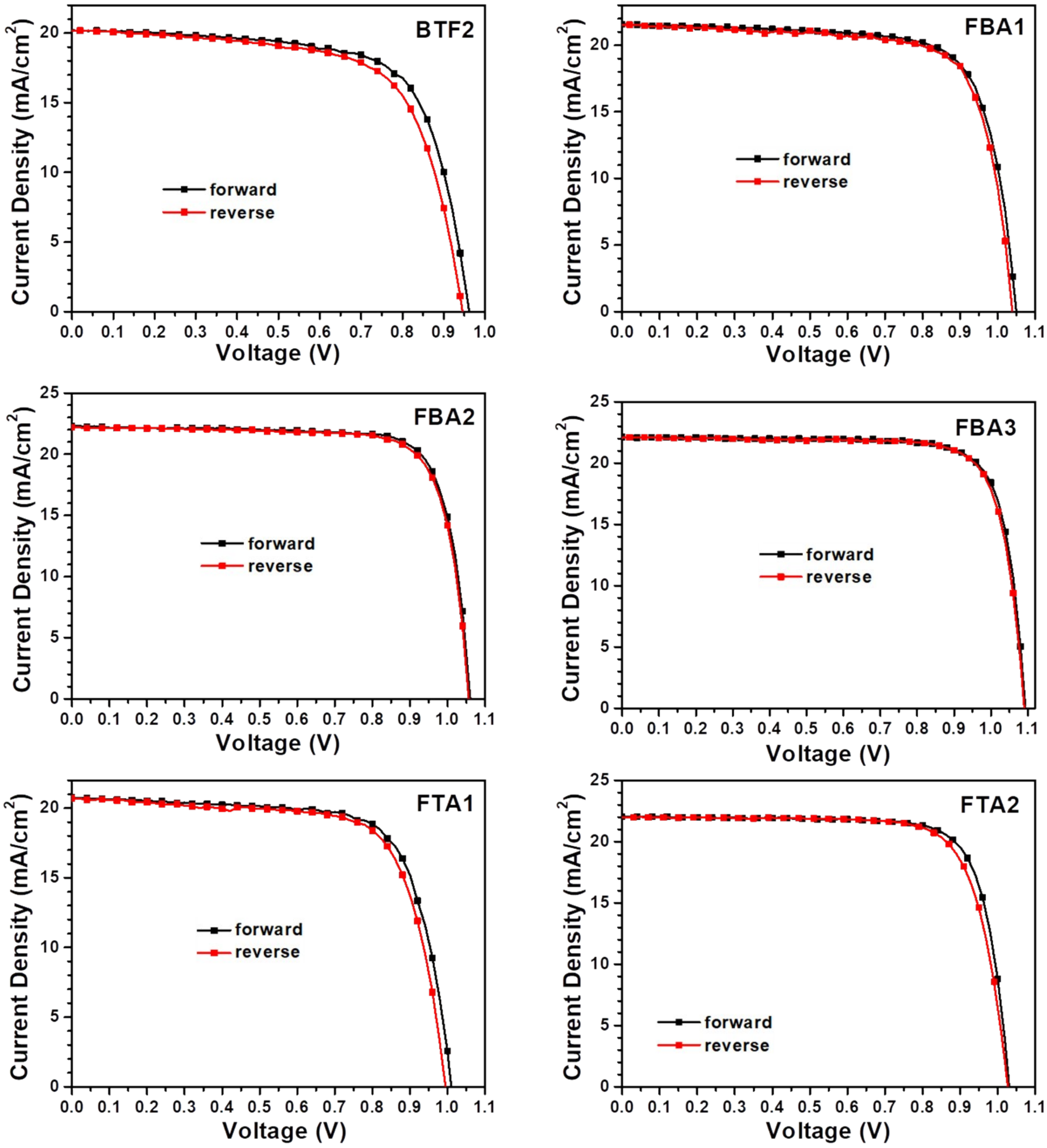
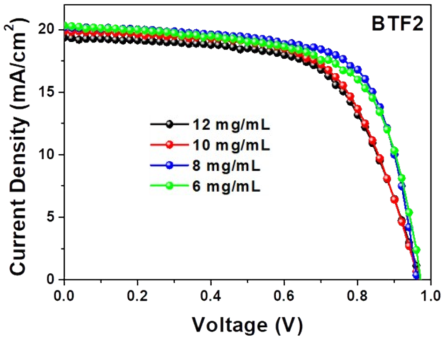


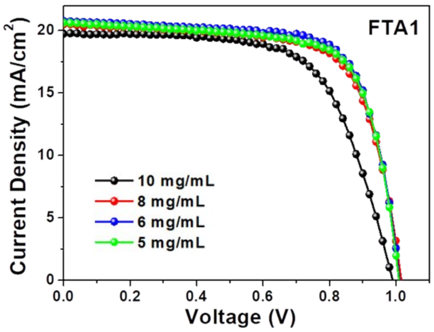
Figure S6. The hole injection characteristics measured by the SCLC method based on a device structure of ITO/PEDOT:PSS/doped Spiro-OMeTAD/MoO_x(10 nm)/Ag.



	V_{oc} (V)		J_{sc} (mA/cm^2)		*FF*(%)		PCE (%)	
	forward	reverse	forward	reverse	forward	reverse	forward	reverse
BTF2	0.96	0.95	20.19	20.18	69.3	66.7	13.44	12.79
FBA1	1.05	1.04	21.57	21.50	74.2	74.2	16.80	16.60
FBA2	1.06	1.06	22.32	22.19	79.0	78.1	18.70	18.36
FBA3	1.09	1.09	22.12	22.06	79.9	79.6	19.27	19.15
FTA1	1.01	0.99	20.76	20.70	72.3	71.8	15.15	14.71
FTA2	1.03	1.03	22.04	21.99	78.1	76.3	17.73	17.29

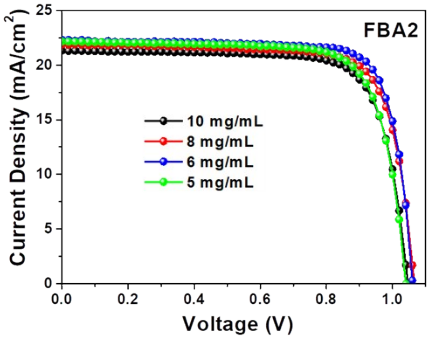
Figure S7. The *J-V* curves and corresponding device parameters of best-performing devices based on dopant-free fluoranthene-cored HTMs under reverse and forward scan

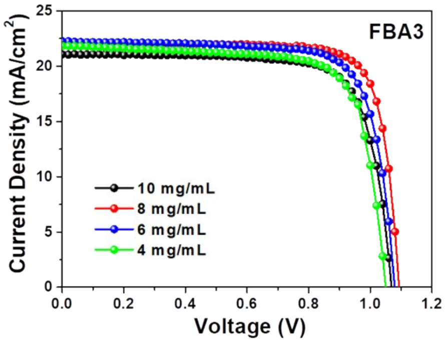




BTF2	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	PCE (%)
12 mg/mL	0.97	19.36	62.6	11.75
10 mg/mL	0.97	19.86	62.7	12.08
8 mg/mL	0.96	20.19	69.3	13.44
6 mg/mL	0.97	20.33	65.6	12.93

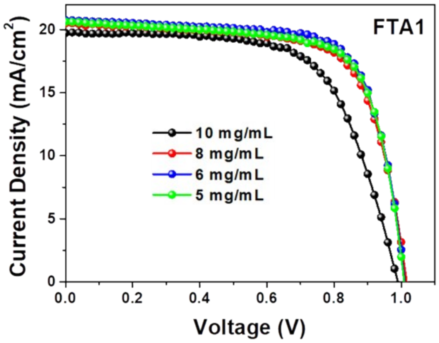
FBA1	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	PCE (%)
10 mg/mL	1.03	20.79	70.4	15.07
8 mg/mL	1.04	21.13	72.2	15.86
6 mg/mL	1.05	21.57	74.2	16.80
5 mg/mL	1.03	21.26	74.0	16.20

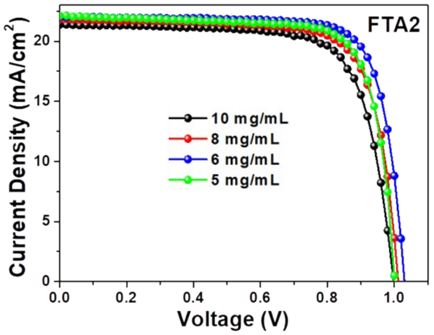




FBA2	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	PCE (%)
10 mg/mL	1.05	21.33	75.7	16.96
8 mg/mL	1.07	21.88	76.6	17.93
6 mg/mL	1.06	22.32	79.0	18.70
5 mg/mL	1.04	22.17	75.9	17.51

FBA3	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	PCE (%)
10 mg/mL	1.07	21.07	76.0	17.13
8 mg/mL	1.09	22.12	79.9	19.27
6 mg/mL	1.08	22.26	76.1	18.30
4 mg/mL	1.05	21.84	74.5	17.08





FTA1	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	PCE (%)
10 mg/mL	0.99	19.75	64.80	12.67
8 mg/mL	1.02	20.50	69.58	14.55
6 mg/mL	1.01	20.76	72.25	15.15
5 mg/mL	1.01	20.64	71.28	14.86

FTA2	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	PCE (%)
10 mg/mL	1.00	21.38	73.7	15.75
8 mg/mL	1.01	21.83	75.5	16.64
6 mg/mL	1.03	22.04	78.1	17.73
5 mg/mL	1.00	22.13	77.0	17.03

Figure S8. The *J-V* curves and corresponding device parameters of PVSCs based on dopant-free fluoranthene-cored HTMs processed by different concentrations.

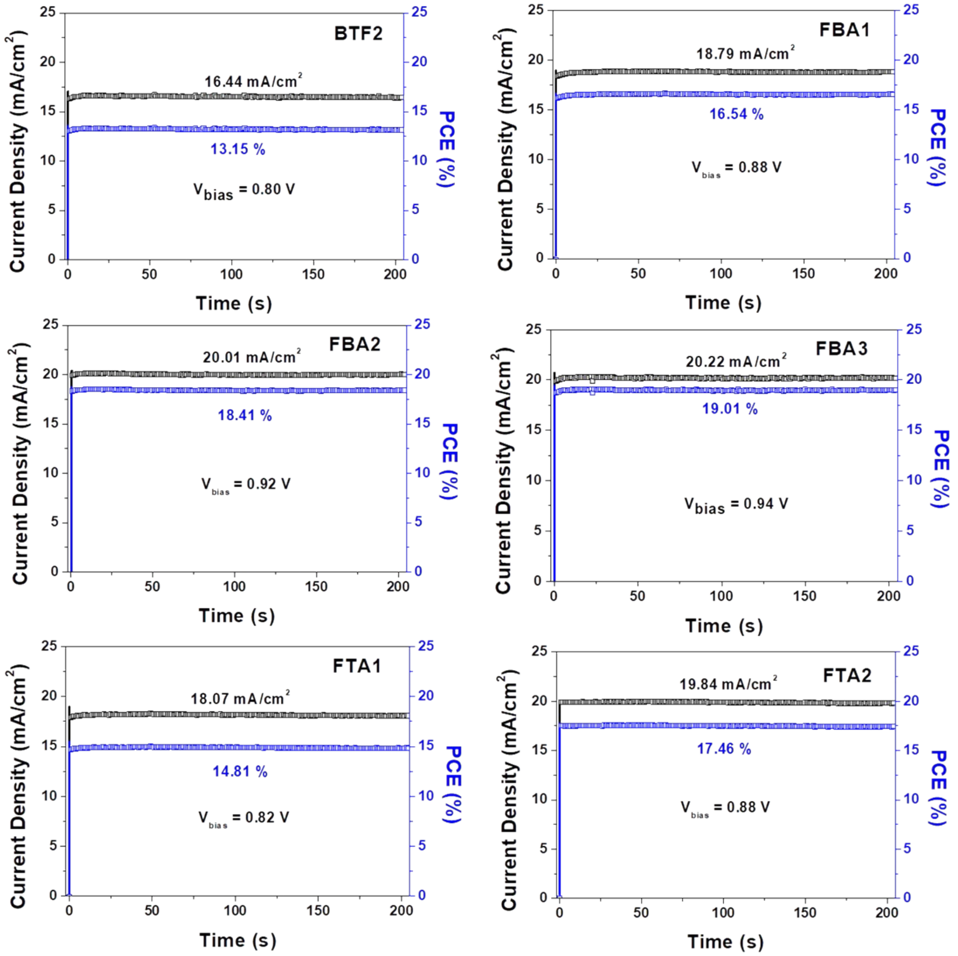


Figure S9. Power output near maximum power point tracking for 200 s, starting from forward bias and resulting in a stabilized power output of 13.15%, 16.54%, 18.41%, 19.01%, 14.81% and 17.46% for **BTF2**, **FBA1**, **FBA2**, **FBA3**, **FTA1** and **FTA2** -based devices, respectively.

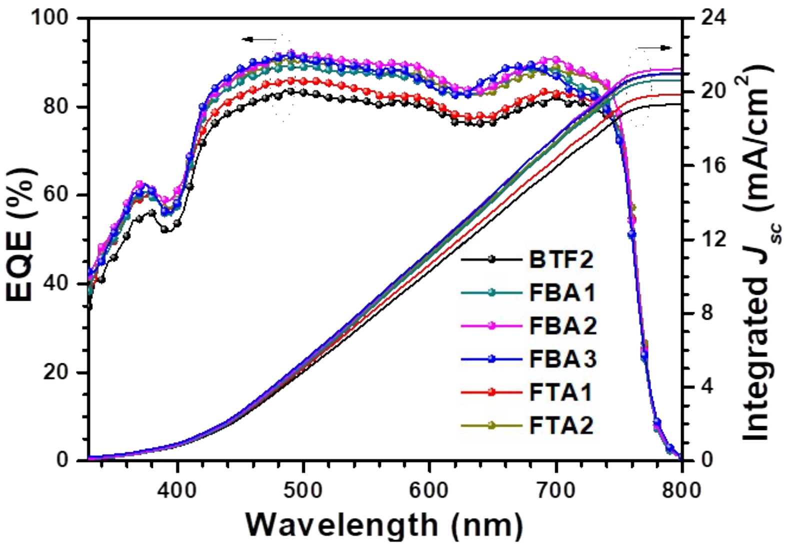


Figure S10. IPCE spectra of PVSCs based on dopant-free fluoranthene-cored HTMs. The integrated J_{sc} values are determined to 19.32 mAcm^{-2} for **BTF2**; 20.65 mAcm^{-2} for **FBA1**; 21.24 mAcm^{-2} for **FBA2**; 21.01 mAcm^{-2} for **FBA3**; 19.85 mAcm^{-2} for **FBA3**; 20.96 mAcm^{-2} for **FTA2**.

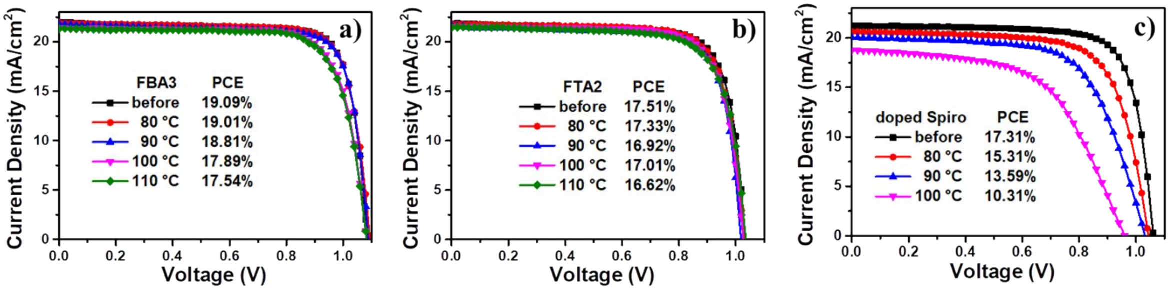


Figure S11. *J–V* curves of the PVSCs with different dopant-free **FBA3** (a) and **FTA2** (b) and doped Spiro-OMeTAD (c) successively heated at different temperature for 20 min in a nitrogen ambience. Note that the measurements were carried out at room temperature.

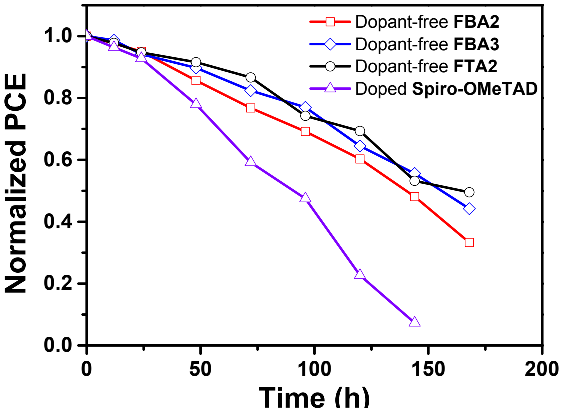


Figure S12. Environmental stability of PVSCs based on dopant-free **FBA2**, **FBA3** and **FTA2** and doped Spiro-OMeTAD performed in ambient air with a humidity of 80%.

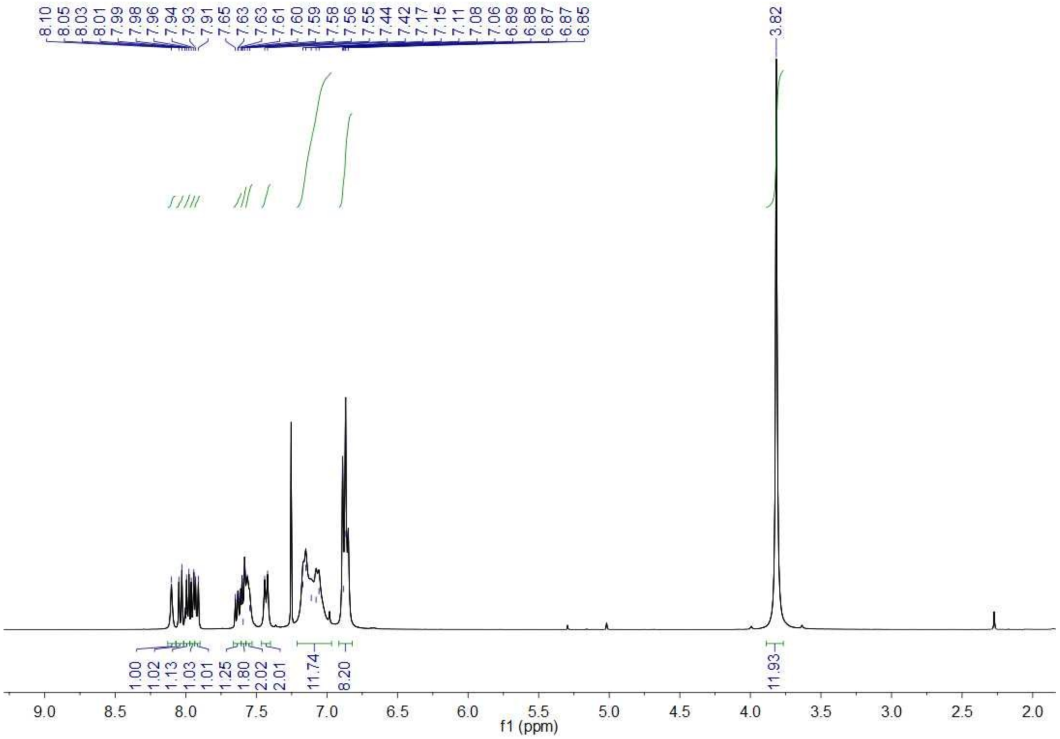


Figure S13. The ^{1}H NMR spectrum of **FBA1**, conducted in Chloroform-*d*.

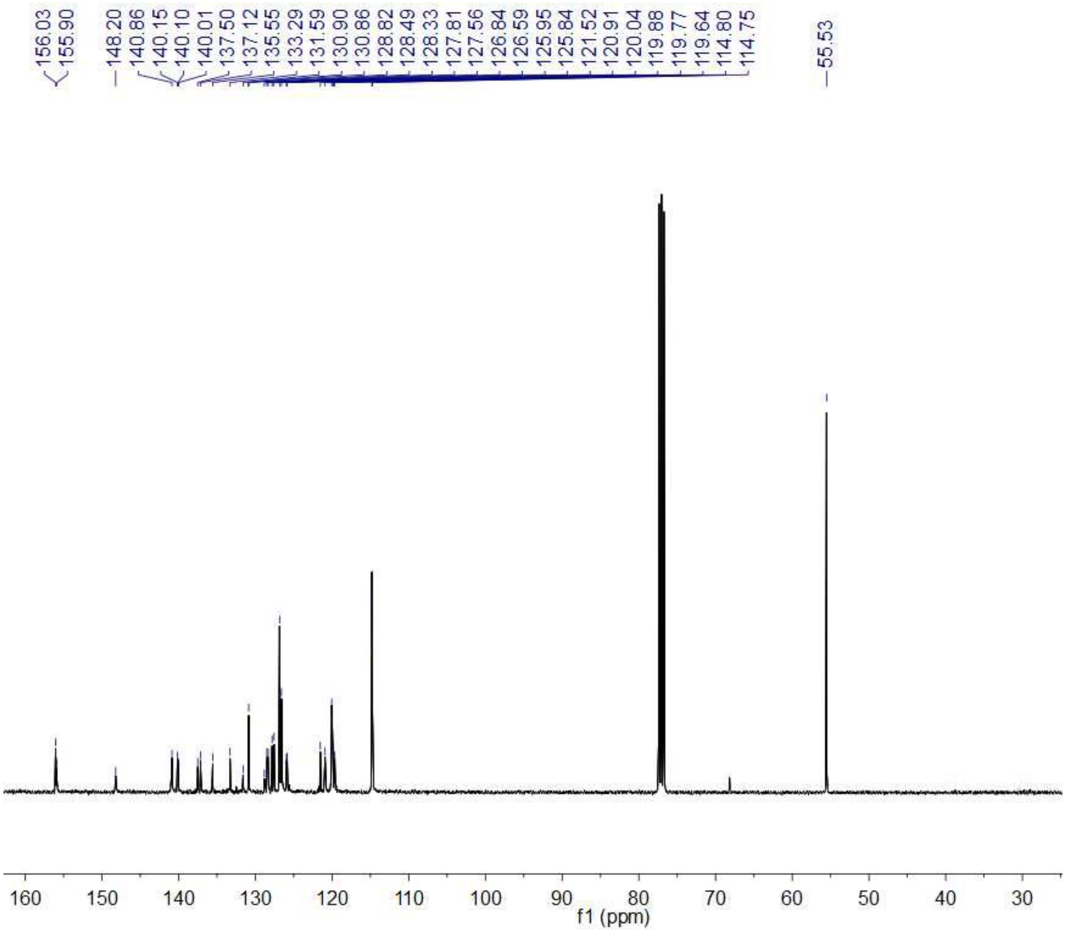


Figure S14. The ^{13}C NMR spectrum of **FBA1**, conducted in Chloroform-*d*.

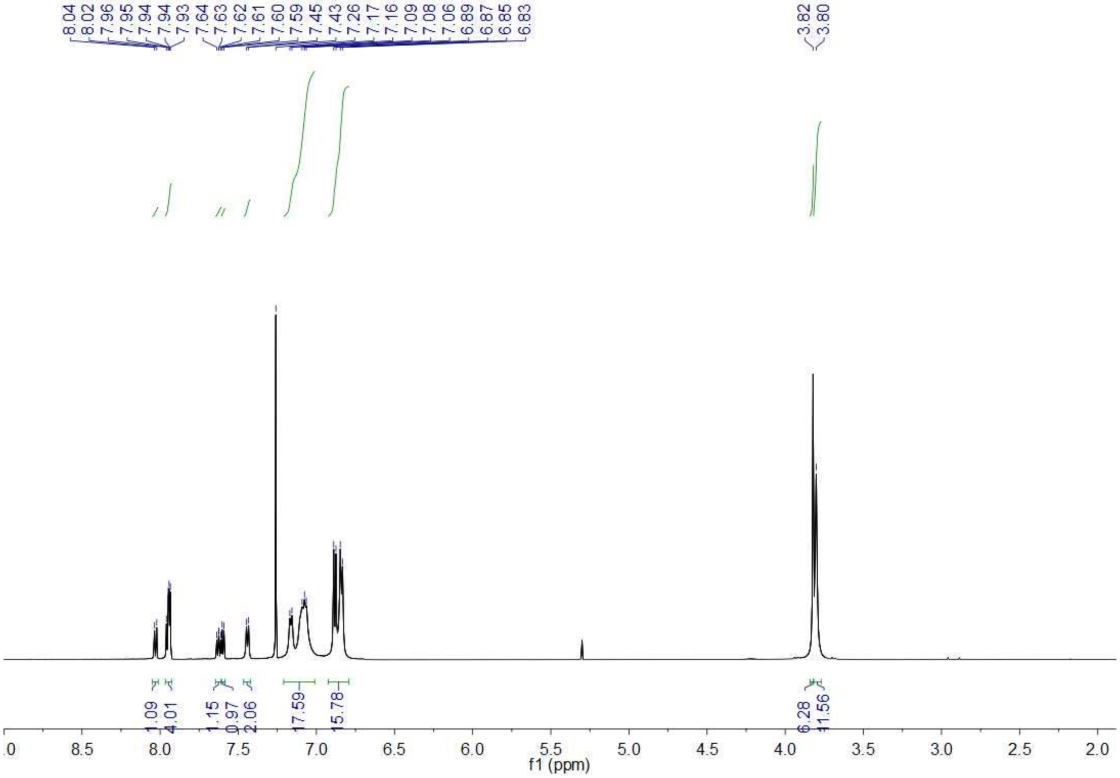


Figure S15. The ^{1}H NMR spectrum of **FTA1**, conducted in Chloroform-*d*.

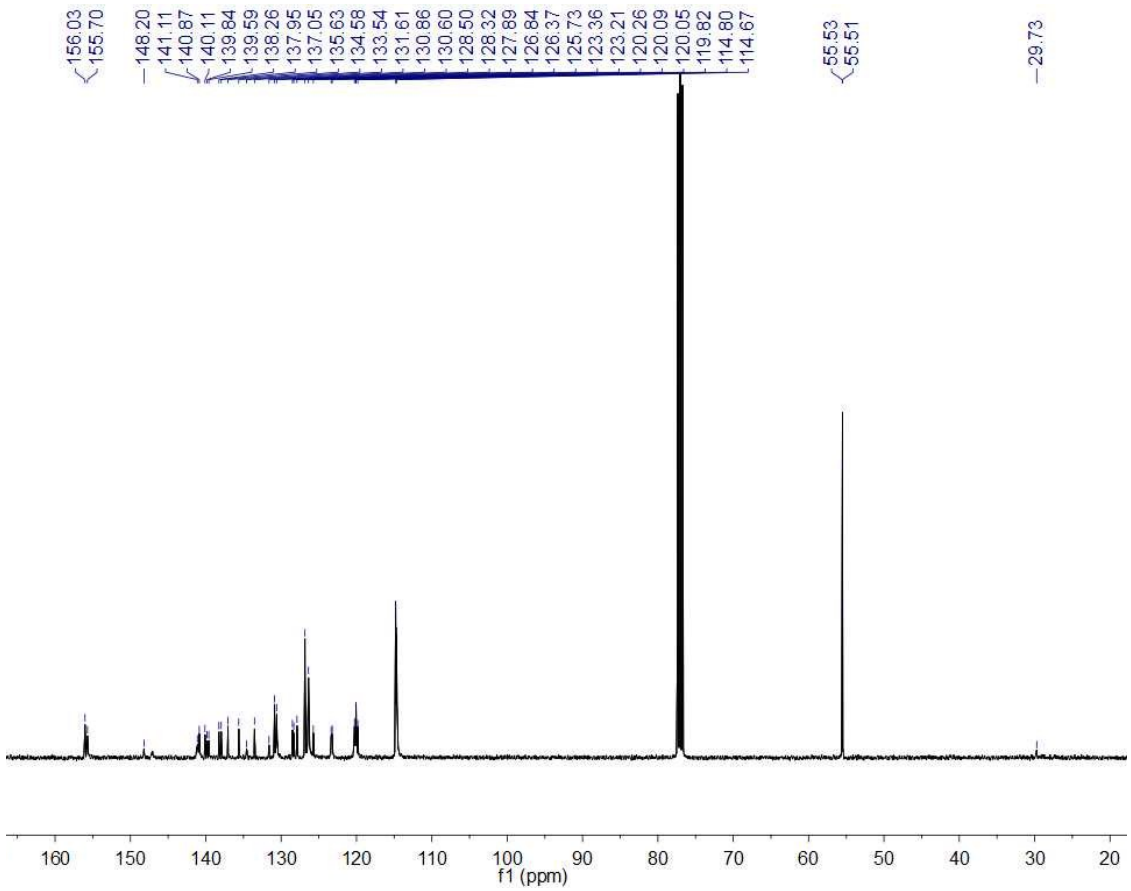


Figure S16. The ^{13}C NMR spectrum of **FTA1**, conducted in Chloroform-*d*.

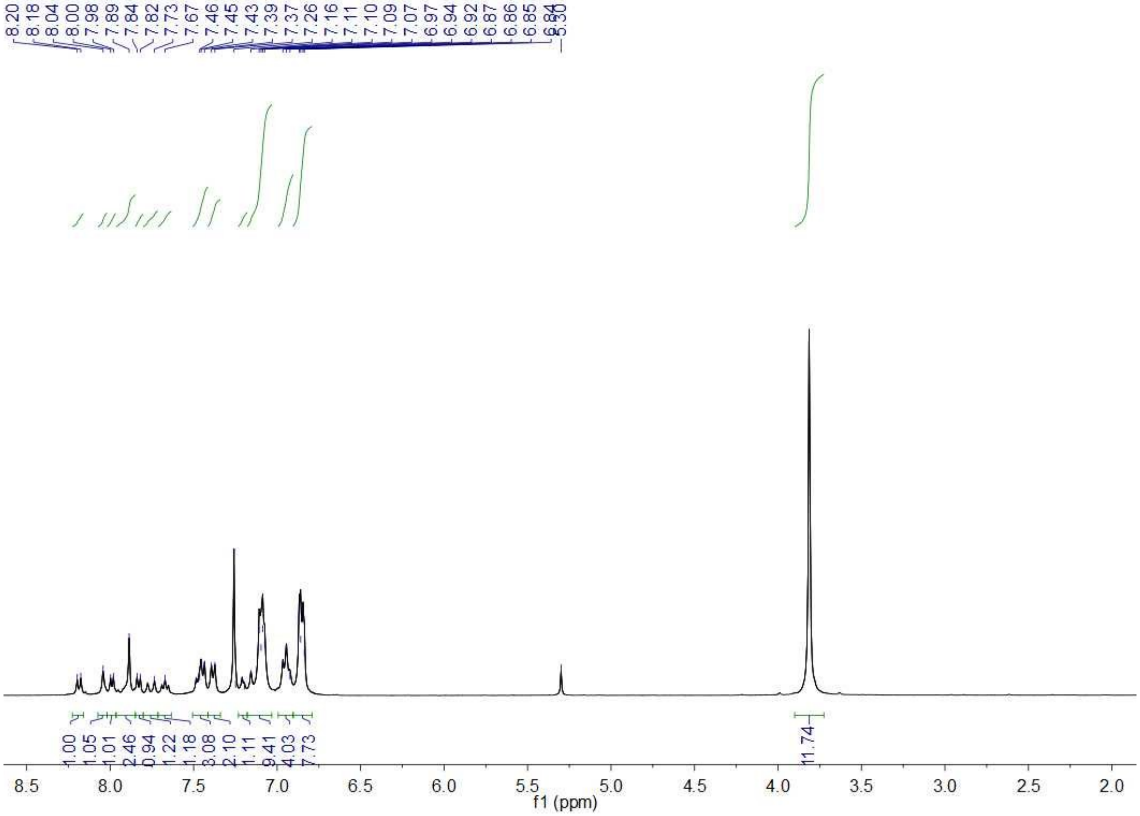


Figure S17. The ^{1}H NMR spectrum of **FBA2**, conducted in Chloroform-*d*.

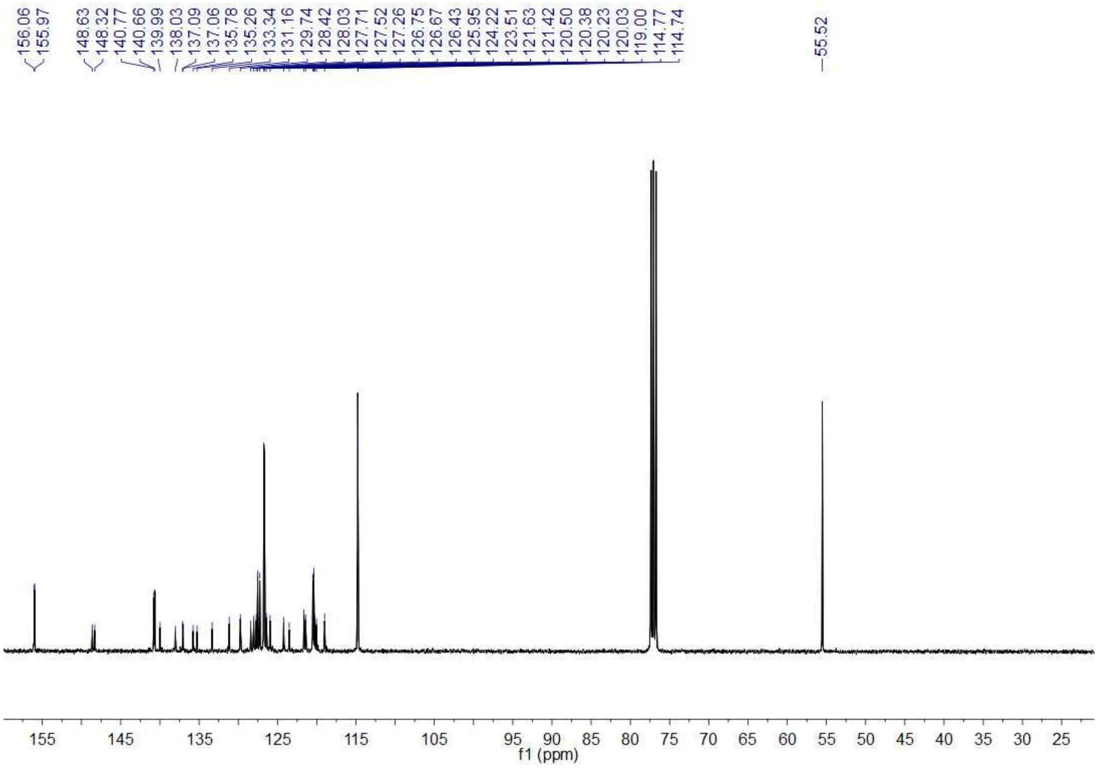


Figure S18. The ^{13}C NMR spectrum of **FBA2**, conducted in Chloroform-*d*.

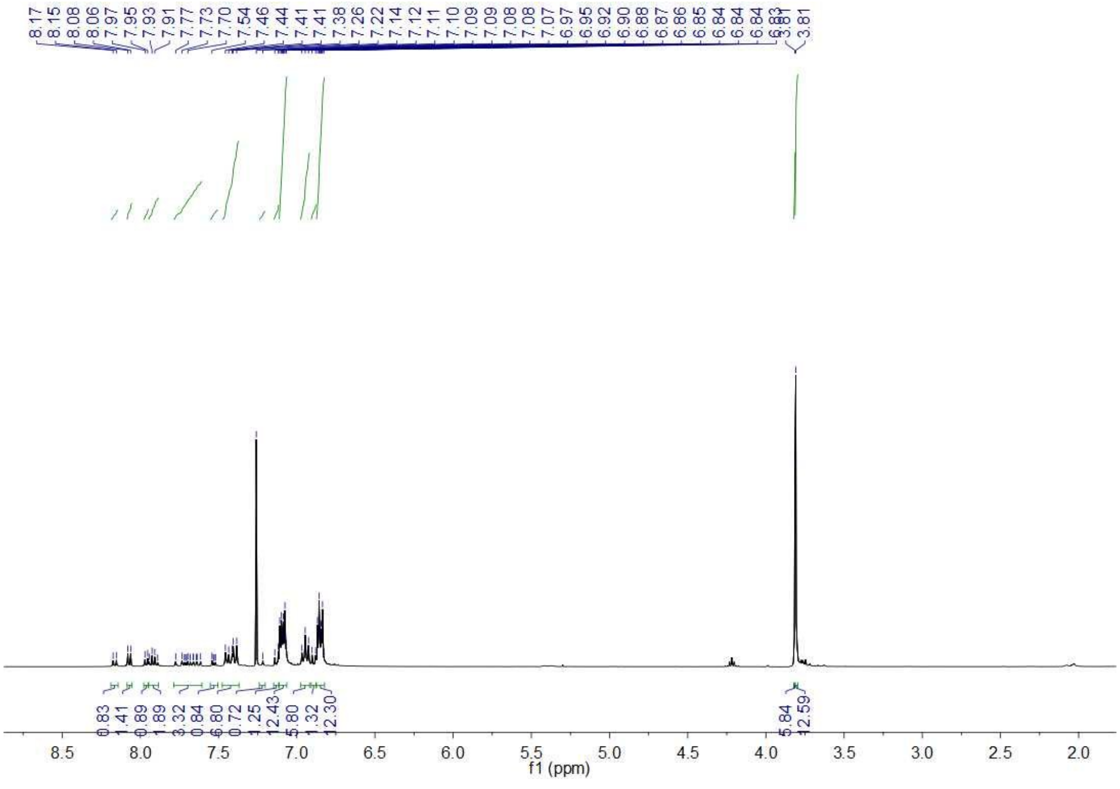


Figure S19. The ^{1}H NMR spectrum of **FTA2**, conducted in Chloroform-*d*.

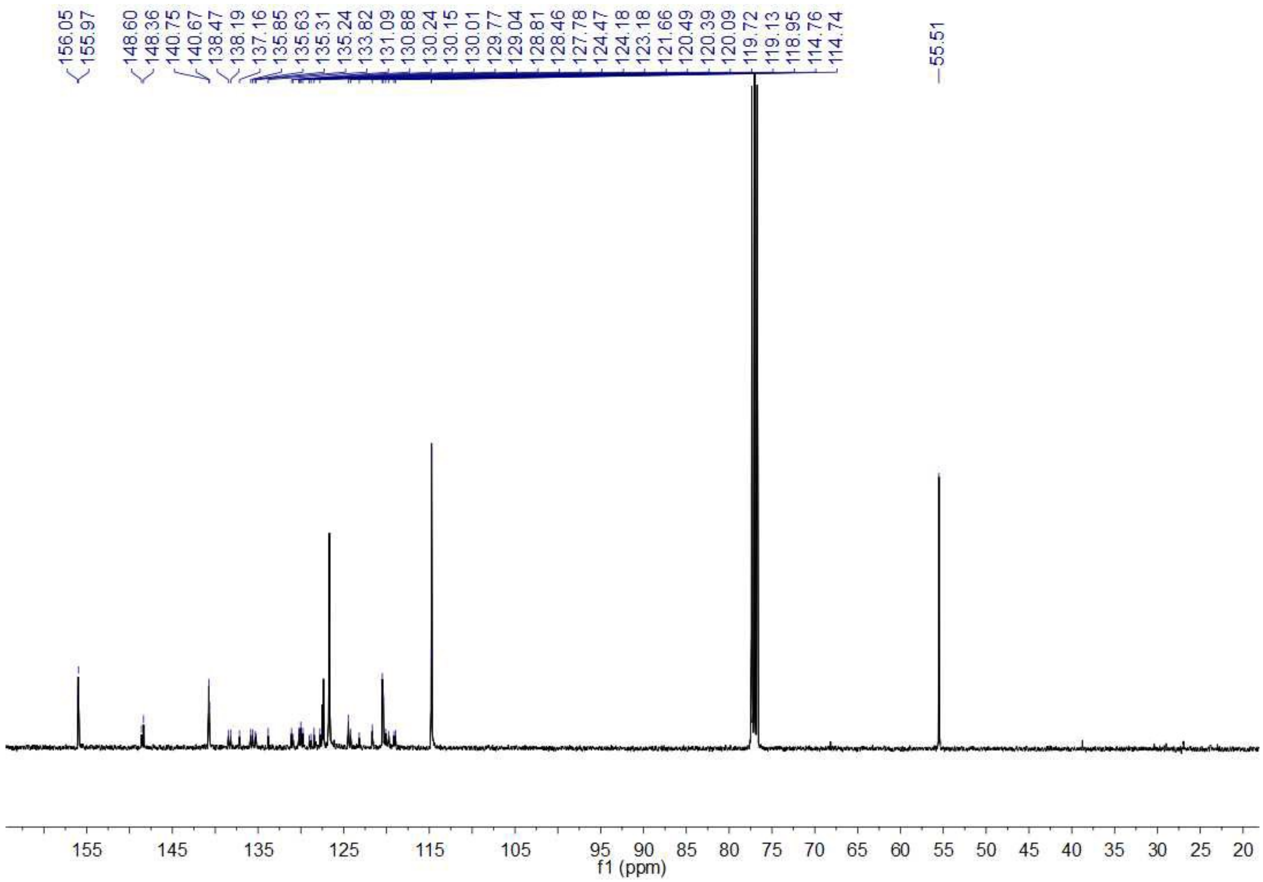


Figure S20. The ^{13}C NMR spectrum of **FTA2**, conducted in Chloroform-*d*.

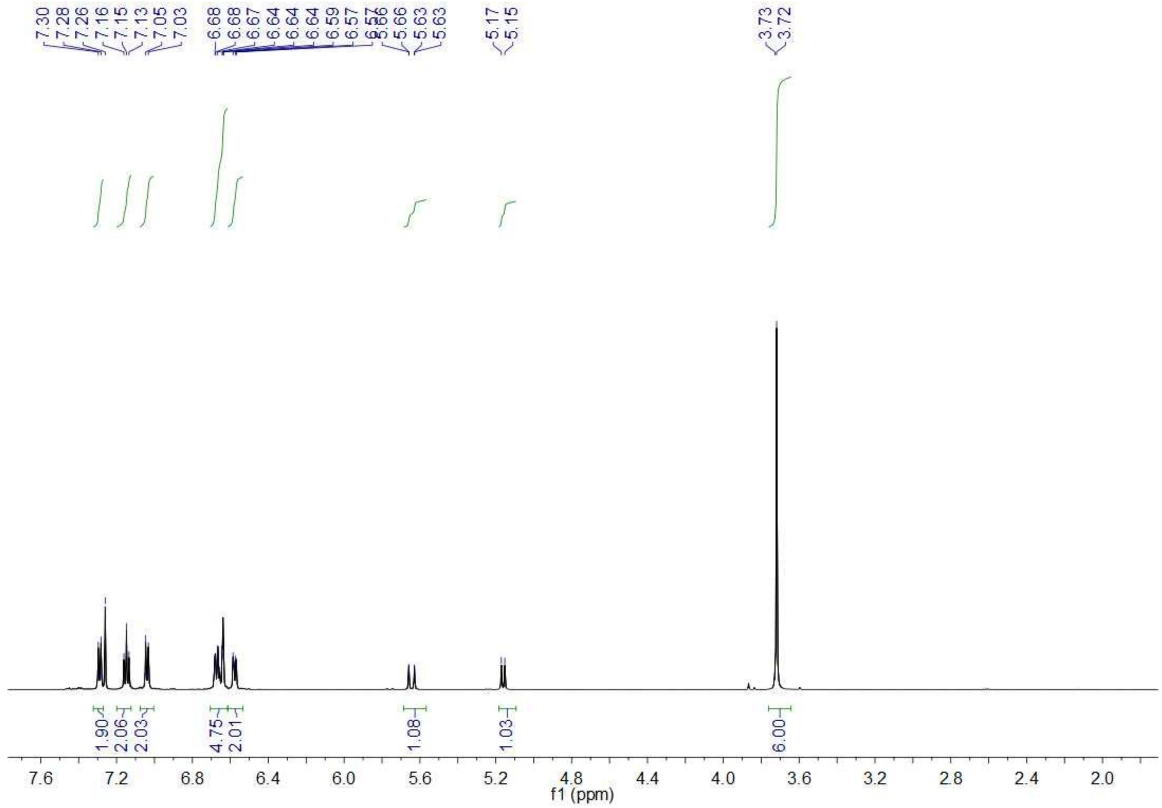


Figure S21. The ^{1}H NMR spectrum of **7**, conducted in Chloroform-*d*.

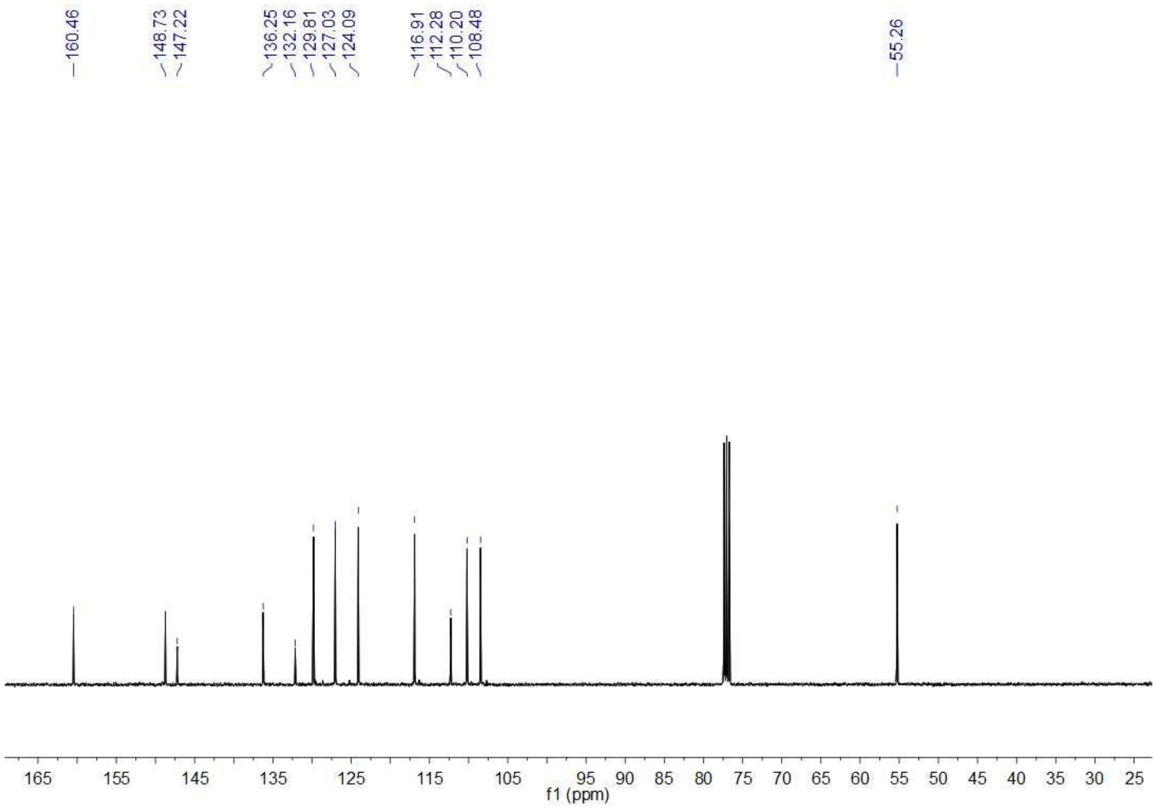


Figure S22. The ^{13}C NMR spectrum of **7**, conducted in Chloroform-*d*.

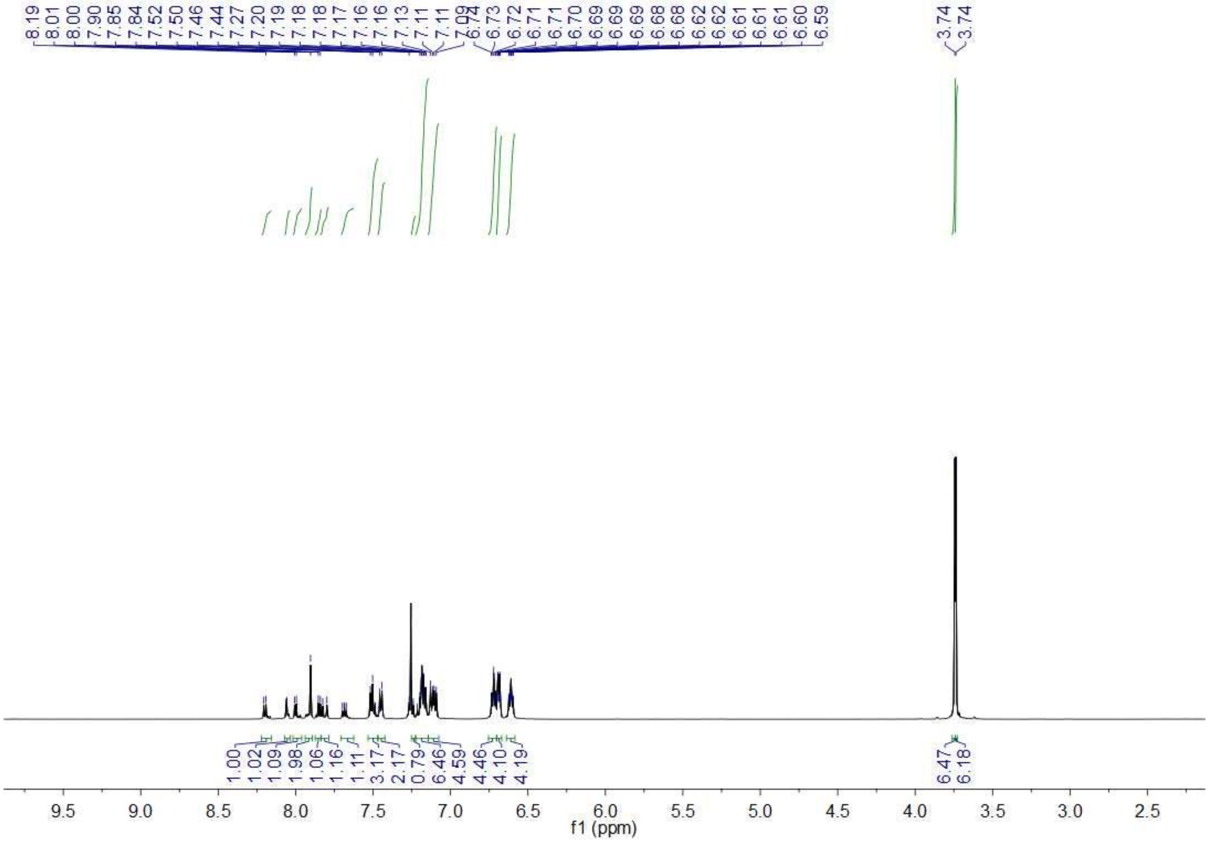


Figure S23. The ^{1}H NMR spectrum of **FBA3**, conducted in Chloroform-*d*.

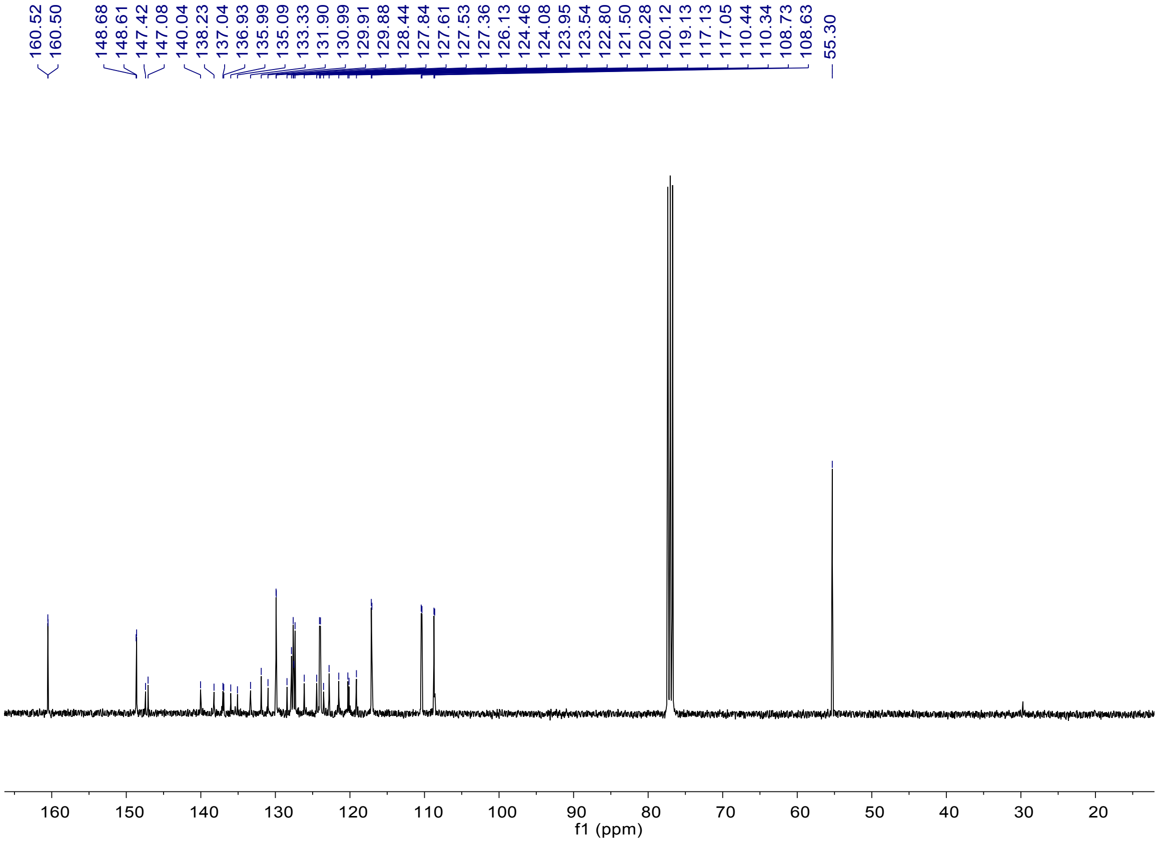


Figure S24. The ^{13}C NMR spectrum of **FBA3**, conducted in Chloroform-*d*.

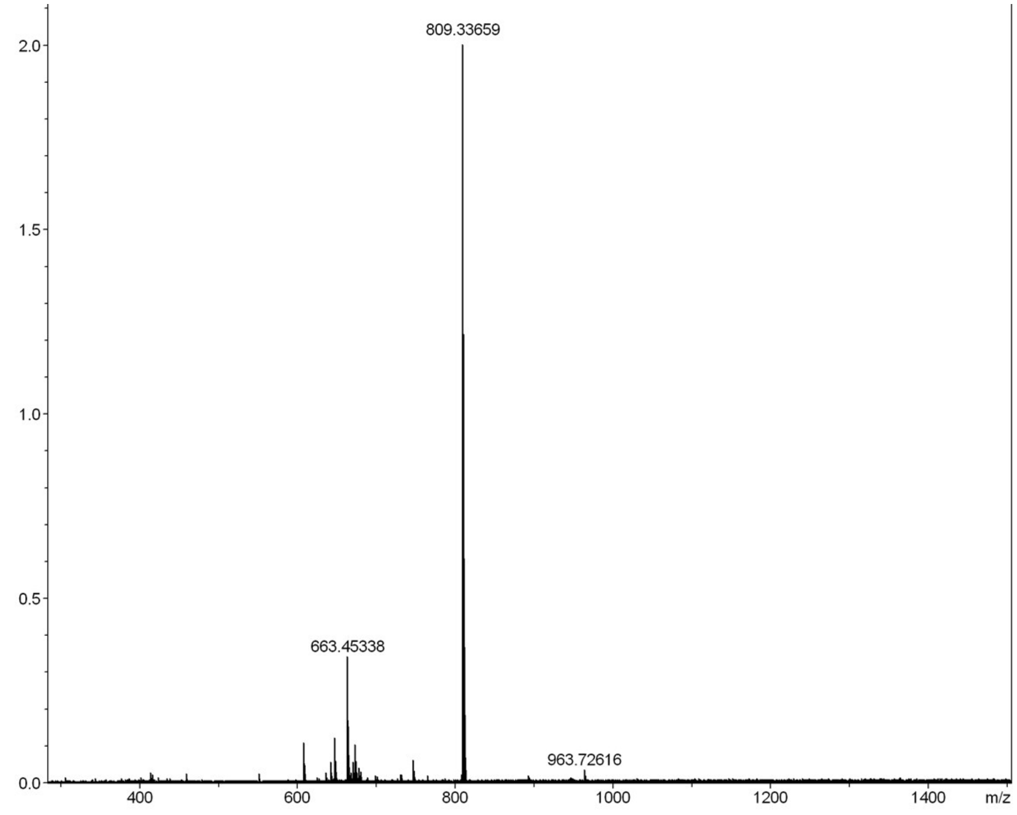


Figure S25. HR-Mass spectrum of **FBA1**.

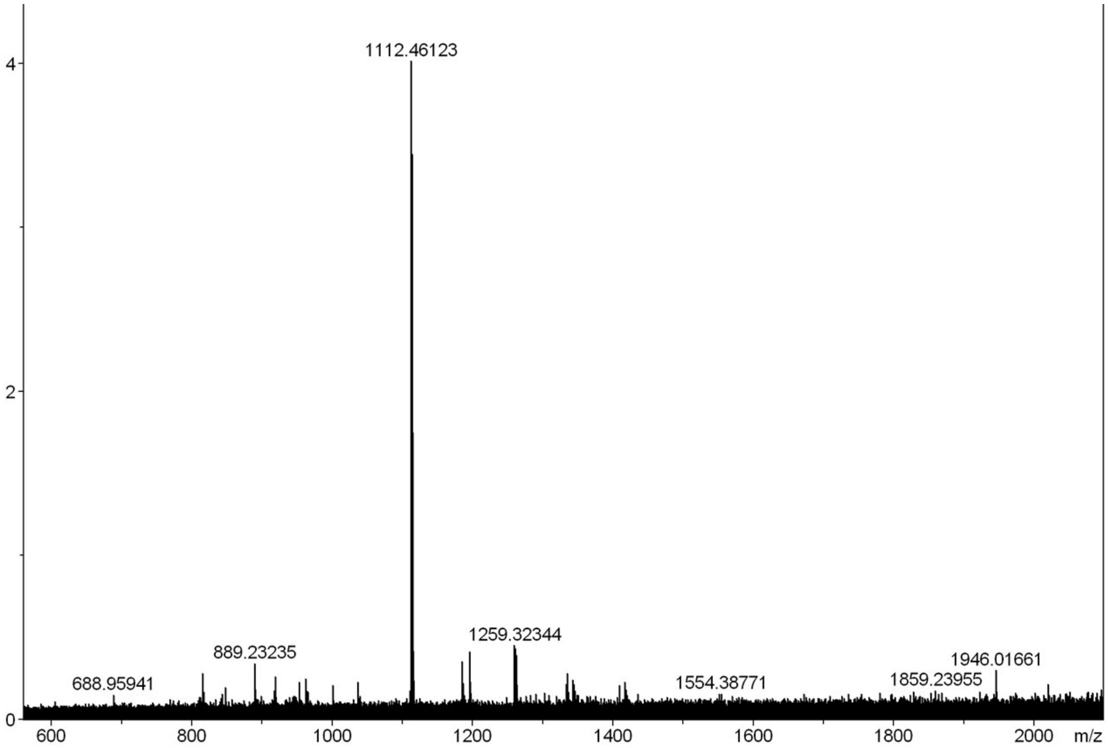


Figure S26. HR-Mass spectrum of **FTA1**.

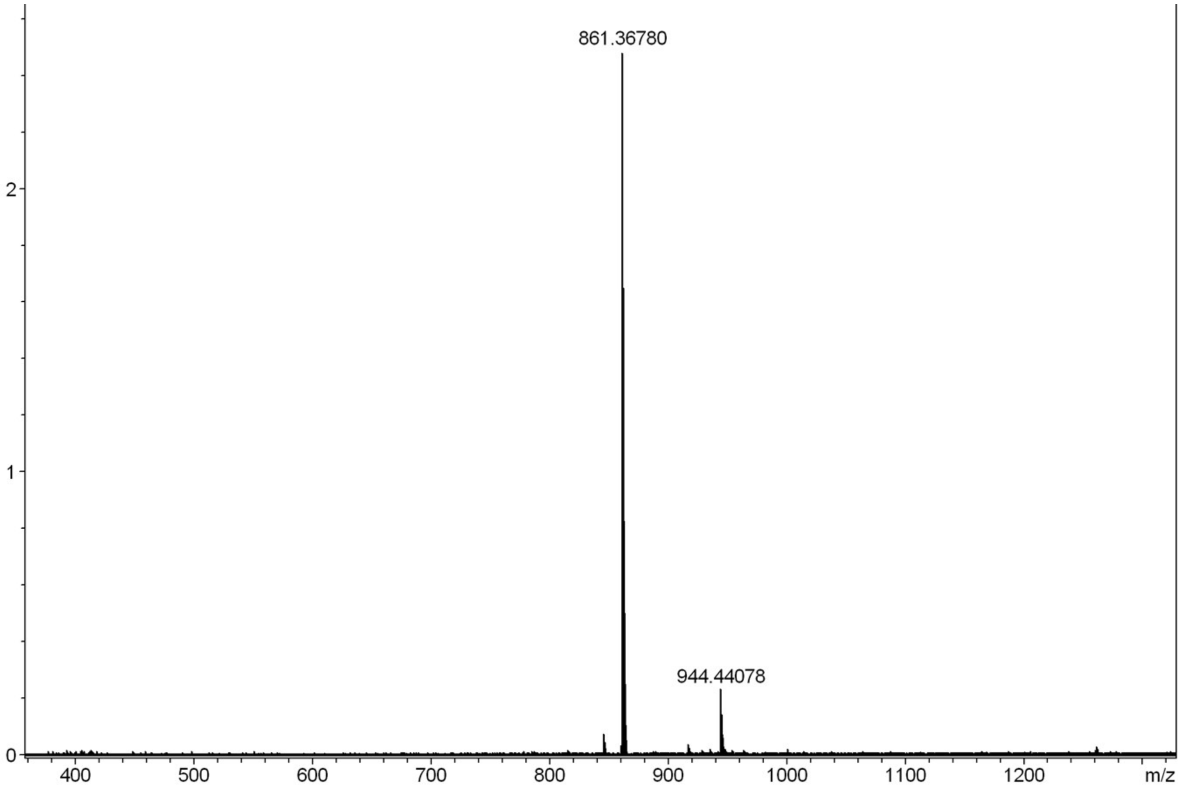


Figure S27. HR-Mass spectrum of **FBA2**

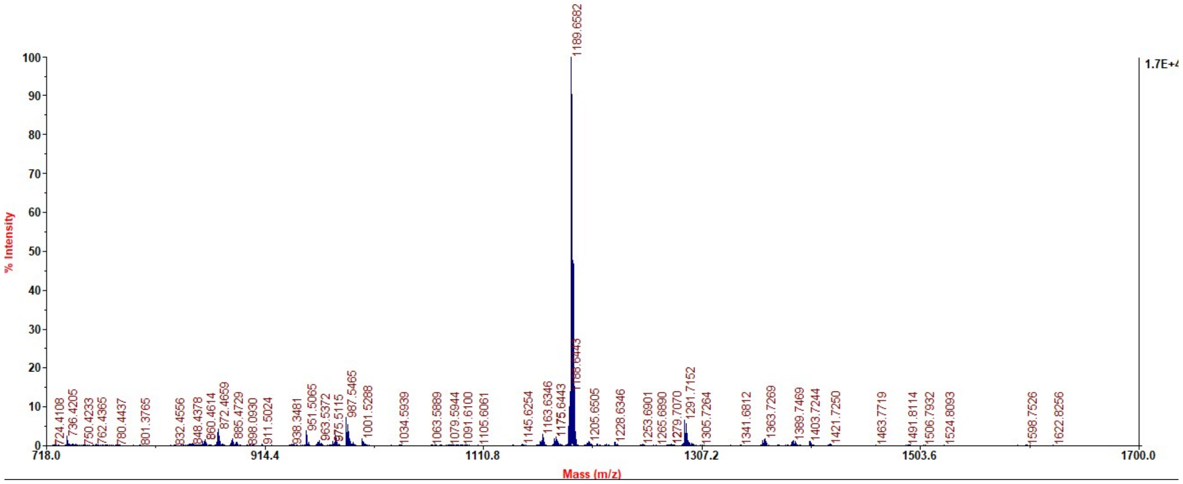


Figure S28. MALDI-TOF-MS spectrum of **FTA2**.

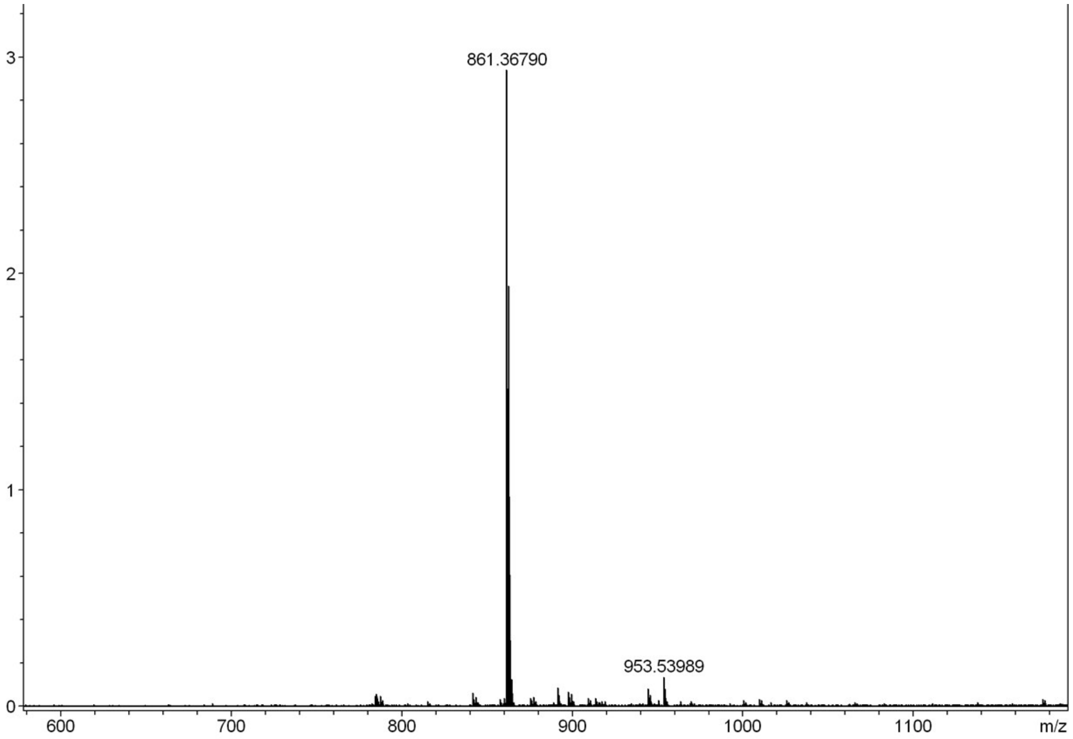


Figure S29. HR-Mass spectrum of **FBA3**.

Reference

1. Knölker, H.-J.; Forke, R.; Krahl, M.; Däbritz, F.; Jäger, A. *Synlett* **2008**, *2008* (12), 1870-1876.

2. Schroot, R.; Schubert, U. S.; Jäger, M. *Macromolecules* **2015**, *48* (7), 1963-1971.

3. Im, Y.; Lee, J. Y. Chemistry of Materials 2014, 26 (3), 1413-1419.