Supplementary Information (SI) for Journal of Materials Chemistry A.

Electronic supplementary information (ESI)

Heteroatom Engineering of *Ortho*-Fluorinated Triarylamine based Hole Transport Materials for Enhanced Performance in Perovskite Solar Cells

Telugu Bhim Raju,*[a] Motonori Watanabe,[abcd] Zhanglin Guo,[acd] Pangpang Wang,[e] Sunao Yamada,[e] Mengde Zhai,[af] and Toshinori Matsushima*[abcd]

[a] *International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka 819-0395, Japan. E-mail: tmatusim@i2cner.kyushu-u.ac.jp*

[b] *Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 819-0395, Japan.*

[c] *Department of Automotive Science, Graduates School of Integrated Frontier Sciences, Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan*

[d] *Center for Energy Systems Design (CESD), International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka 819-0395, Japan*

[e] *Materials Open Lab., Institute of Systems, Information Technologies and Nanotechnologies (ISIT), Fukuoka 814-0001, Japan*

[f] *Institute for Energy, Research School of Energy and Power Engineering, Jiangsu University, Zhenjiang 212013, China.*

*Corresponding authors: Telugu Bhim Raju, Toshinori Matsushima,

Email: tmatusim@i2cner.kyushu-u.ac.jp

Email: bhimraju@i2cner.kyushu-u.ac.jp

1. Experimental section

1.1. Materials and methods.

All solvents and chemicals were purchased from Aldrich, Tokyo Chemical Industry, and Wako chemicals with a purity of more than 98%. Thin-layer chromatography (TLC) was performed using Merck KGaA precoated TLC Silica Gel 60F254 aluminum sheets. Column chromatography was carried out using glass columns packed with Silicycle UltraPure SilicaFlash P60 silica gel (40–63 μm, 230–400 mesh). Unless otherwise stated, all reactions and manipulations were conducted under a nitrogen atmosphere. Reagent-grade solvents were used for synthesis, while spectroscopy-grade solvents were used for spectral measurements. All solvents were dried using standard procedures.

1.2. Characterizations

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 600 MHz spectrometer in deuterated chloroform ($CDCl_3$), using tetramethylsilane (TMS) as an internal standard. Chemical shifts were referenced to the deuterated solvent ($CDCl_3$: δ = 7.26 ppm for ^{1}H and δ = 77.23 ppm for ^{13}C). All spectra were obtained at room temperature, with chemical shifts reported in ppm and coupling constants in Hz. Mass spectrometry analysis was conducted using an ultra-performance liquid chromatography time-of-flight mass spectrometer (UPLC-TOF-MS, Agilent 1290-6545). NMR and mass spectra are presented in Figures S2–S22. UV–VIS–NIR absorption spectra were measured for both solution-state (dichloromethane) and thin-film samples (fabricated on quartz substrates) using a Jasco V-730 spectrophotometer. Steady-state photoluminescence (PL) spectra and time-resolved transient PL decays of the perovskite and HTM films were measured using a steady-state PL spectrometer (FP-8300, JASCO) and a PL lifetime spectrometer (Quantaurus-Tau, Hamamatsu Photonics), respectively. Photoelectron yield spectroscopy (PYS, AC-2, Rikenkeiki) was performed to measure the energy levels of the perovskite and HTM thin films. For PYS measurements, doped and undoped HTMs were prepared by dissolving 56 mg of each compound in 1 mL of chlorobenzene, followed by spin-coating the resulting solutions onto ITO substrates. The ground-state geometries and vertical excitation energies of the synthesized HTM molecules were investigated using density functional theory (DFT) and time-dependent DFT (TD-DFT). All calculations were performed with the B3LYP functional and the 6-

31G(d,p) basis set, without applying any solvent model, as implemented in the Gaussian 16 software package. AFM of the HTM films was performed using an ICONIR AFM system (tapping mode, Bruker) equipped with an antimony-doped Si tip with a reflective Au coating (spring constant: 42 N m^{-1}). The scan area was 10 × 10 μm^2. Top-view SEM images of the perovskite films were obtained using a field-emission SEM system (JSM-7900F, JEOL) at an acceleration voltage of 5 kV and a magnification of ×10,000.

1.3. Synthetic procedure

All reagents and chemicals, including compounds 1 and 2, as well as 3-fluoroaniline, 3,3'-dibromo-2,2'-bithiophene, and other reagents in Fig. S1, were purchased from commercial suppliers and used without further purification. Solvents were purified by standard procedures and dried when necessary. The starting materials, intermediate compounds, and the target compounds 3–8 and 13 were synthesized according to our previously reported procedure, while the remaining compounds were characterized by NMR spectroscopy.[S1–S11]

Scheme:

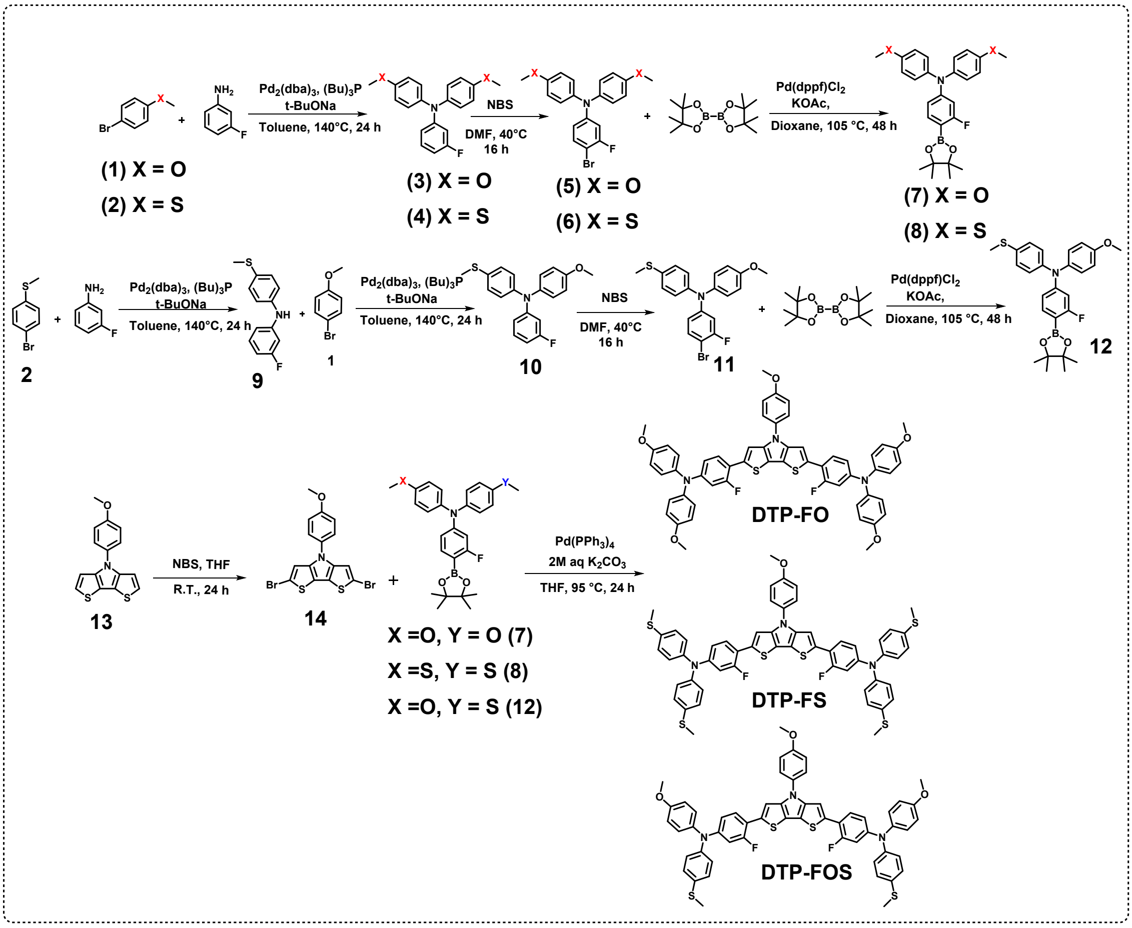


Fig. S1. Synthetic routes of the three HTMs.

Synthesis of 3-fluoro-N,N-bis(4-methoxyphenyl)aniline (3) or 3-fluoro-N,N-bis(4-(methylthio)phenyl)aniline (4)

A solution of 3-fluoroaniline (44.9 mmol), 4-bromothioanisole or 4-bromoanisole (112.5 mmol), t-BuONa (269 mmol), and $P(t\text{-}Bu)_3$ (1.8 mmol) in dry toluene (80 mL) was degassed under nitrogen for 30 minutes. $Pd_2(dba)_3$ (0.45 mmol) was then added under a nitrogen atmosphere, and the reaction mixture was refluxed for 48 hours. After cooling to room temperature, the crude product was extracted using chloroform, washed with water, and concentrated under reduced pressure.

Compound 3 was obtained as a brown solid through column chromatography (hexane/chloroform, 2:1, v/v). Yield- 72%. ^1H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, J = 8.7 Hz, 4H), 7.06 (d, J = 8.7 Hz, 4H), 6.87 (d, J = 8.2 Hz, 1H), 6.81 (d, J = 11.8 Hz, 1H), 6.71 (t, J = 7.8 Hz, 1H), 3.99 (s, 6H); ^{13}C NMR (151 MHz, CDCl3) δ 164.37, 162.76, 156.38, 150.68, 148.62, 140.26, 129.90, 127.17, 125.41, 115.31 – 114.76, 113.84, 106.62 – 106.24, 106.23, 77.37, 77.16, 76.95, 55.43.

Compound 4 was obtained as a light green liquid and purified by column chromatography (hexane/chloroform, 3:1, v/v). Yield- 70%. ^1H NMR (600 MHz, $CDCl_3$) δ 7.20 – 7.17 (m, 4H), 7.14 (dd, J = 15.0, 8.2 Hz, 1H), 7.05 – 7.00 (m, 4H), 6.80 – 6.76 (m, 1H), 6.74 – 6.68 (m, 1H), 6.64 (d, J = 2.3 Hz, 1H), 2.48 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.39, 162.77, 149.37, 144.72, 132.96, 130.26, 128.50, 125.46, 118.05, 109.58, 109.42, 108.95, 108.81, 77.37, 77.16, 76.95, 16.75.

Synthesis of 4-bromo-2-fluoro-N,N-bis(4-methoxyphenyl)aniline (5) or 4-bromo-3-fluoro-N,N-bis(4-(methylthio)phenyl)aniline (6)

Toward the solution of compound 3 or 4 (1g, 3.09 mmol) in DMF (50 mL) was added with NBS (0.66g, 3.71 mmol) at 0°C. The reaction mixture was moved to room temperature and then stirred at 40°C for 16 h in dark, which was quenched by water and extracted with chloroform. The solvent of organic phase was removed, and the residue was purified column chromatography (hexane/chloroform, 2:1, v/v).

Compound 5 was obtained as a pale green viscous oil. Yield- 90%. ^1H NMR (600 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 4H), 7.10 (d, J = 8.6 Hz, 12H), 6.88 (d, J = 8.7 Hz, 12H), 6.67 (d, J = 11.2 Hz, 3H), 6.58 (d, J = 8.7 Hz, 3H), 3.81 (s, 18H); ^{13}C NMR (151 MHz, CDCl3) δ 156.66, 149.94, 139.68, 132.99, 127.25, 115.88, 114.98, 107.04, 106.87, 97.62, 97.48, 55.48.

Compound 6 was obtained as a pale green viscous oil. Yield- 92%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 1H), 7.20 – 7.18 (m, 4H), 7.04 – 7.00 (m, 4H), 6.77 (dd, J = 10.8, 2.6 Hz, 1H), 6.70 – 6.65 (m, 1H), 2.48 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.28, 158.65, 148.62, 144.08, 133.68, 133.40, 128.36, 125.58, 124.12, 118.68, 109.98, 109.82, 100.31, 100.16, 77.37, 77.16, 76.95, 16.53.

Synthesis of 3-fluoro-N,N-bis(4-(methyloxy)phenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (7) or 3-fluoro-N,N-bis(4-(methylthio)phenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (8)

Compound **5** or **6** (29.90 mmol) and bis(pinacolato)diborane (44.85 mmol) were dissolved in dry dioxane along with potassium acetate (149.5 mmol) and $Pd(dppf)Cl_2$ (5.98 mmol). With the protection of nitrogen, the mixture was heated to 110°C and kept stirring 48 h. The crude product was obtained via the extracted with chloroform and washed with water, which was purified by column chromatography (Hexane/chloroform, 1:2, v/v).

Compound 7 was obtained as a yellow solid. Yield- 80%. ^{1}H NMR (600 MHz, CDCl3) δ 7.44 (d, J = 7.7 Hz, 1H), 7.04 (d, J = 8.5 Hz, 4H), 6.81 (d, J = 8.5 Hz, 4H), 6.55 (d, J = 8.3 Hz, 1H), 6.42 (d, J = 12.3 Hz, 1H), 3.75 (s, 6H), 1.29 (s, 12H). ^{13}C NMR (151 MHz, CDCl3) δ 169.36, 167.71, 156.84, 153.59, 139.60, 137.30, 127.73, 114.95, 113.55, 104.76, 104.57, 83.61, 83.46, 77.37, 77.16, 76.95, 55.56, 25.13, 24.89.

Compound 8 was obtained as an orange-red solid. Yield- 75%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (dd, J = 8.2, 7.2 Hz, 1H), 7.20 – 7.16 (m, 4H), 7.06 – 7.01 (m, 4H), 6.73 (dd, J = 8.3, 2.1 Hz, 1H), 6.61 (dd, J = 11.9, 2.0 Hz, 1H), 2.48 (s, 6H), 1.34 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.15, 167.49, 152.29, 143.96, 137.45, 133.86, 128.21, 126.11, 116.10, 107.49, 107.31, 83.63, 77.37, 77.16, 76.95, 24.89, 16.45.

Synthesis of 3-fluoro-N-(4-(methylthio)phenyl)aniline (9)

A solution of 3-fluoroaniline (1g, 10.73 mmol), 4-bromothioanisole (2.6g, 12.88 mmol), t-BuONa (2g, 21 mmol), and $P(t\text{-}Bu)_3$ (1.8 mmol) in dry toluene (80 mL) was degassed under nitrogen for 30 minutes. $Pd_2(dba)_3$ (0.1g, 0.10 mmol) was then added under a nitrogen atmosphere, and the reaction mixture was refluxed for 48 hours. After cooling to room temperature, the crude product was extracted using chloroform, washed with water, and concentrated under reduced pressure. **Compound 9** was obtained as a brown liquid through column chromatography (hexane/chloroform, 2:1, v/v). Yield- 70%, 1.46 g. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.38 (m, 3H), 7.27 (m, 1H), 6.95-6.94 (d, 2H), 6.80 (d, 1H), 5.97 (s, 1H), 2.70 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.66, 163.04, 145.34, 139.98, 130.60, 129.43, 119.96, 112.47, 107.21, 107.07, 103.59, 103.42, 17.46.

Synthesis of 3-fluoro-N-(4-methoxyphenyl)-N-(4-(methylthio)phenyl)aniline (10)

Compound **9** (3.5g, 15.02 mmol), 4-bromoanisole (4.2g, 22.53 mmol), t-BuONa (2.8g, 30.0 mmol), and $P(t\text{-}Bu)_3$ (1.8 mmol) in dry toluene (80 mL) was degassed under nitrogen for 30 minutes. $Pd_2(dba)_3$ (0.13g, 0.15 mmol) was then added under a nitrogen atmosphere, and the reaction mixture was refluxed for 48 hours. After cooling to room temperature, the crude product was extracted using chloroform, washed with water, and concentrated under reduced pressure. **Compound 10** was obtained as a yellow liquid through column chromatography (hexane/chloroform, 2:1, v/v). Yield- 80%, 4.03 g. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, 1H), 7.22 – 7.19 (m, 5H), 7.10 (dt, 4H), 7.04 (dd, 4H), 6.88 (dd, 4H), 6.80 – 6.74 (m, 2H), 6.72 – 6.65 (m, 2H), 6.64 – 6.58 (m, 2H), 3.82 (s, 6H), 2.49 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.36, 162.74, 156.76, 149.93, 149.86, 145.18, 139.90, 137.93, 132.03, 130.07, 129.12, 128.58, 128.32, 127.68, 125.39, 124.67, 116.76, 115.01, 108.27, 108.10, 107.91, 107.76, 55.53, 16.87.

Synthesis of 4-bromo-3-fluoro-N-(4-methoxyphenyl)-N-(4-(methylthio)phenyl)aniline (11)

Compound **10** (5g, 14.7 mmol) in DMF (80 mL) was added with NBS (3.14g, 17.67 mmol) at 0°C. The reaction mixture was moved to room temperature then stirred at 40°C for 16 h in dark, which was quenched by water and extracted with chloroform. The crude compound was used further any purification.

Synthesis of 3-fluoro-N-(4-methoxyphenyl)-N-(4-(methylthio)phenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (12)

Compound **10** (5g, 11.95 mmol) and bis(pinacolato)diborane (4.5g, 17.92 mmol) were dissolved in dry dioxane along with potassium acetate (3.51g, 35.85 mmol) and Pd(dppf)Cl_2 (0.43g, 0.597 mmol) with the protection of nitrogen, the mixture was heated to 110°C and kept stirring 48 h. The crude product was obtained via the extracted with chloroform and washed with water, which was purified by column chromatography (Hexane/chloroform, 1:2, v/v). Yield- 75%, 4.17 g. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, 1H), 7.18 (d, 2H), 7.12 – 7.01 (m, 4H), 6.87 (s, 2H), 6.68 (s, 1H), 6.55 (d, 1H), 3.81 (d, 3H), 2.48 (d, 3H), 1.35 (d, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.22, 167.57, 157.07, 152.85, 144.31, 139.27, 137.36, 133.19, 128.26, 128.04, 125.63, 114.99, 106.26, 106.07, 83.54, 55.54, 25.11, 24.88, 16.58.

Synthesis of 2,6-dibromo-4-(4-methoxyphenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole] (14)

4-(4-Methoxyphenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (**13**) (0.5 g, 1.75 mmol) was dissolved in dry THF (100 mL), then *N*-Bromo succinimide (0.72 g, 4.02 mmol) was added at 0°C. The reaction mixture was stirred at 0°C for 15 min in dark, then solution temperature was raised up to 30°C and kept stirring for 24 h. After completion of the reaction, the crude product was quenched by water and extracted with chloroform. The residue was purified column chromatography (Hexane/chloroform, 3:1, v/v) to afford compound **(14)** as a white solid (Yield- 96%, 0.75 g). ^{1}H NMR (600 MHz, CDCl3) δ 7.38 (d, J = 8.4 Hz, 2H), 7.08 (s, 2H), 7.03 (d, J = 8.4 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.56, 141.28, 132.04, 124.68, 116.22, 115.35, 115.19, 110.42, 77.37, 77.16, 76.95, 55.78.

General synthesis of HTMs

Suzuki coupling reaction (DTP-FO, DTP-FS and DTP-FOS): Organo boronate (2.5 eq), compound 14 (1 eq), 2 M K_2CO_3 (aq), and Pd(PPh_3)$_4$ (4 mol%) were added to a 50 mL reaction flask. Tetrahydrofuran (THF, 20 mL) was then added under a nitrogen atmosphere. The reaction mixture was heated to 85°C and stirred for 24 h under nitrogen. After cooling to room temperature, the mixture was concentrated, and the residue was extracted with chloroform and water. The organic layer was dried over $MgSO_4$, and the solvent was removed via rotary evaporation. The crude product was purified by silica gel column chromatography.

Synthesis of 4,4'-(4-(4-methoxyphenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole-2,6-diyl)bis(3-fluoro-N,N-bis(4-methoxyphenyl)aniline) (DTP-FO)

Compound DTP-FO was synthesized via a Suzuki reaction and subsequently purified by column chromatography using chloroform, yielding an orange-red solid with a 72% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, 2H), 7.38 (d, 2H), 7.33 (s, 2H), 7.08 (dd, 10H), 6.89 – 6.83 (m, 8H), 6.64 (ddd, 4H), 3.88 (s, 3H), 3.81 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.46, 160.09, 158.82, 158.02, 157.07, 156.59, 153.31, 149.15, 145.90, 144.54, 139.94, 132.90, 128.32, 127.30, 124.67, 115.28, 115.06, 114.96, 109.70, 106.76, 106.59, 55.62.

Synthesis of 4,4'-(4-(4-methoxyphenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole-2,6-diyl)bis(3-fluoro-N,N-bis(4-(methylthio)phenyl)aniline) (DTP-FS)

Compound DTP-FS was synthesized via a Suzuki reaction and subsequently purified by column chromatography using chloroform, yielding an orange solid with a 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.40 (m, 4H), 7.38 (s, 2H), 7.20 (t, J = 6.8 Hz, 8H), 7.04 (dd, J = 11.6, 5.0 Hz, 8H), 6.78 (dd, J = 15.5, 11.1, 2.1 Hz, 4H), 3.89 (s, 3H), 2.48 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.14, 133.37, 132.66, 128.33, 125.58, 124.57, 117.82, 115.05, 109.36, 77.37, 77.16, 76.95, 55.68, 16.56.

Synthesis of 4,4'-(4-(4-methoxyphenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole-2,6-diyl)bis(3-fluoro-N-(4-methoxyphenyl)-N-(4-(methylthio)phenyl)aniline) (DTP-FOS)

Compound DTP-FOS was synthesized via a Suzuki reaction and subsequently purified by column chromatography using chloroform, yielding an orange solid with a 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.40 (dd, 5H), 7.21 – 7.18 (m, 4H), 7.09 – 7.02 (m, 10H), 6.89 – 6.85 (m, 4H), 6.73 (ddd, 4H), 3.88 (s, 3H), 3.82 (s, 6H), 2.48 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.36, 158.72, 158.05, 156.91, 148.25, 144.71, 139.52, 132.78, 132.48, 128.49, 128.36, 127.74, 124.93, 124.66, 116.82, 115.36, 115.07, 110.02, 108.38, 108.21, 55.61, 16.81.

2. Device Fabrication

2.1 Materials

The SnO_2 colloidal dispersion (15% in H_2O) was purchased from Alfa Aesar. Formamidinium hydroiodide (FAI), lead iodide (PbI_2), and methylammonium chloride (MACl) were obtained from Tokyo Chemical Industry. Chlorobenzene (CB), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetonitrile, spiro-MeOTAD, 4-tert-butylpyridine (4-tBP), lithium bis(trifluoromethylsulfonyl)imide (LiTFSI), and tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) tri[bis(trifluoromethane)sulfonimide] (FK-209) were purchased from Sigma-Aldrich. ITO-coated glass substrates were supplied by Atsugi Micro.

2.2 Preparation of perovskite solutions

To prepare precursor solution for two-step deposition of the $FAPbI_3$ perovskite layer, 691 mg PbI_2 was dissolved in DMF: DMSO = 9:1 (at a volume ratio, 1 ml) at room temperature. The mixed organic salt precursor solution was prepared by adding 90 mg FAI and 12 mg MACl in 1 ml IPA and stirred at 25°C for 3 hours.

2.3 Device fabrication detail

Glass substrates coated with a pre-patterned ITO layer (~150 nm, Atsugi Micro; sheet resistance ~10 Ω sq^{-1}) were sequentially cleaned with detergent, deionized water, acetone, and anhydrous isopropanol for 10 min each. The cleaned substrates were then exposed to UV–ozone treatment for 15 min prior to use. A thin SnO_2 nanoparticle layer was deposited by spin-coating a colloidal SnO_2 dispersion (diluted with deionized water at a 1:3 volume ratio) at 3000 rpm for 30 s, followed by annealing at 150 °C for 30 min. After cooling to room temperature, the substrates underwent an additional 15 min UV–ozone treatment before transfer into an N_2-filled glovebox. The perovskite active layer was fabricated using a two-step deposition method. First, a PbI_2 film was deposited by spin-coating a PbI_2 precursor solution onto the SnO_2-coated substrates at 1500 rpm for 30 s, followed by annealing at 70 °C for 1 min. Subsequently, a mixed FAI/MACl organic salt solution was spin-coated onto the PbI_2 layer at 1800 rpm for 30 s, and the resulting films were annealed at 150 °C for 15 min under ambient conditions (20–30% relative humidity). For the HTM layer, either 36 mg of spiro-MeOTAD or 28 mg of DTP-based HTMs was dissolved in 0.5 mL of chlorobenzene, together with 15 μL of 4-tert-butylpyridine, 8.6 μL of a Li-TFSI solution (520 mg mL^{-1} in acetonitrile), and 14.6 μL of an FK-209 solution (300 mg mL^{-1} in acetonitrile). The doped HTM solution was then spin-coated onto the perovskite film at 3000 rpm for 30 s. Finally, an ~80 nm thick Au electrode was thermally evaporated through a shadow mask under high vacuum (~10^{-4} Pa) at a deposition rate of ~0.1 nm s^{-1}, yielding an active device area of 0.12 cm^2. For photovoltaic characterization, the illuminated area was precisely defined as 0.0956 cm^2 by means of a metal shadow mask with openings. For long-term operational stability measurements, the PSCs were encapsulated with a glass lid and sealed along the perimeter using a UV-curable epoxy. The encapsulant was subsequently hardened under UV irradiation. This sealing procedure effectively protected the devices from oxygen ingress and ambient humidity during stability testing.

2.4 Solar cell performance measurement

All *J*–*V* characteristics of the devices were recorded using a computer-controlled Keysight B2901A source/measure unit under simulated AM1.5G solar illumination provided by a Xe-lamp-based solar simulator (HAL-320, Asahi Spectra). Measurements were conducted in the backward scan mode at a scan rate of 200 mV s^{-1}, with the voltage step maintained at 0.05 V. The light intensity was carefully calibrated to 100 mW cm^{-2} using a crystalline Si reference cell equipped with an amorphous Si optical filter (Bunko-Keiki), certified by the National Institute of Advanced Industrial Science and Technology (AIST), Japan. For operational stability assessments, *J*–*V* curves of encapsulated PSCs were periodically recorded under continuous white LED illumination at 100 mW cm^{-2} (PAS-100, System Engineers), with the devices held at their maximum power point between scans. External quantum efficiency (EQE) curves of PSCs were obtained with the Keysight B2901A source/measure unit and a constant-energy monochromatic light source (PVL-5000, Asahi Spectra). To calculate EQE, the monochromatic light energy was measured using a power meter (843-R, Newport) and an optical power detector (818-UV/DB, Newport).

3.1 Hole mobility and hole conductivity measurements

The hole mobility of the HTM layers was determined using the space-charge-limited current (SCLC) method with a structure of ITO/undoped HTM/MoO_3/Al. J–V characteristics were measured in the range of 0–4 V and fitted wwith the SCLC model according to

$$J = \frac{9\varepsilon_0 \varepsilon_r \mu_h V^2}{8L^3},$$

where J is the current density, L is the HTM layer thickness, $\mu_h$is the hole mobility, ε_r is the relative dielectric constant of the transport medium (a typical value is 3 for organic materials, and therefore we used this value), and ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}). The internal device voltage is denoted as V.

Conductivity measurements employed a structure of ITO/doped HTM/MoO_3/Al. The electrical conductivity in the chemically doped HTM films was obtained from the J–V slopes using a conventional Ohm law.

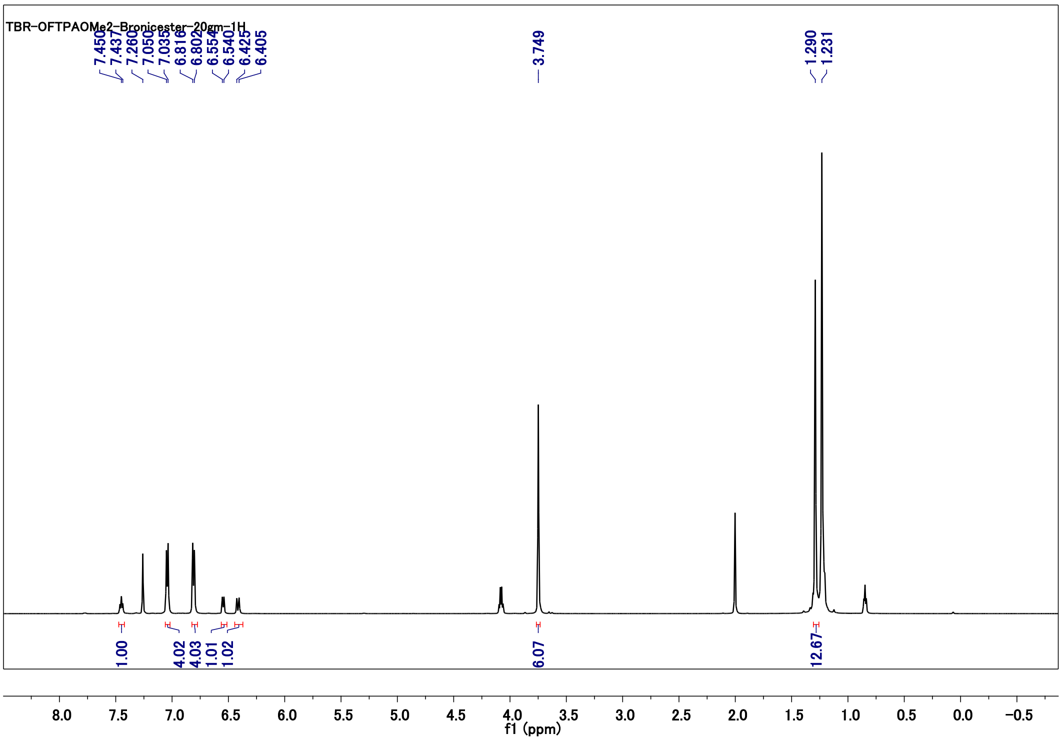


Fig. S2. ^{1}H NMR spectrum of compound 7 in deuterated chloroform.

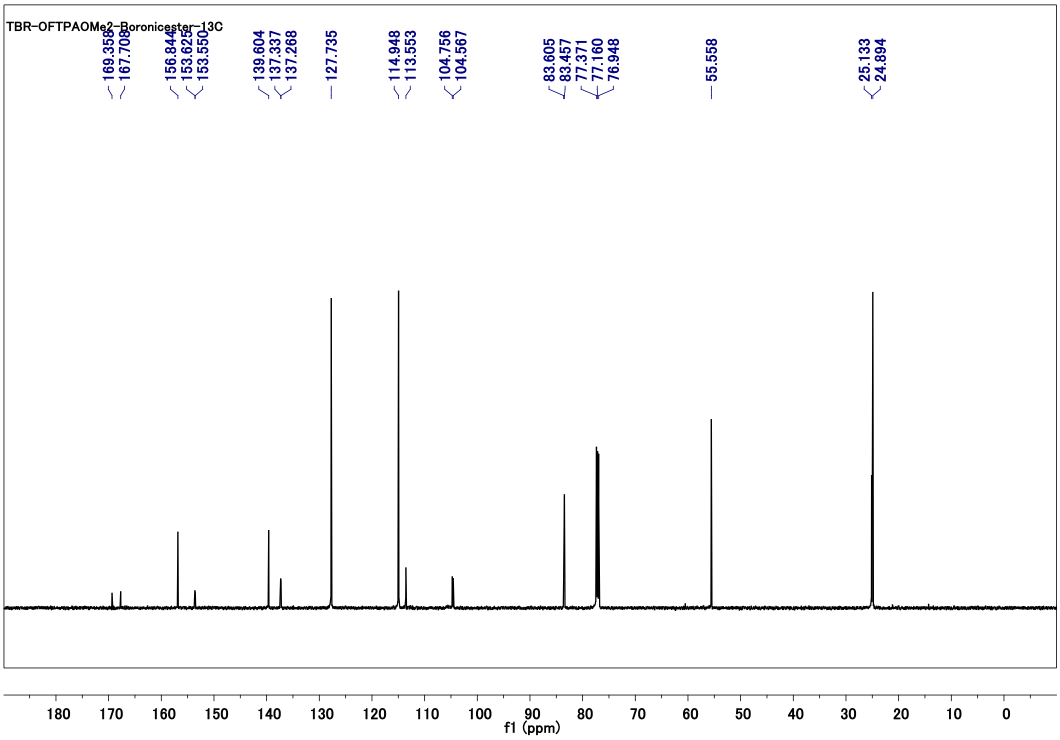


Fig. S3. ^{13}C NMR spectrum of compound 7 in deuterated chloroform.

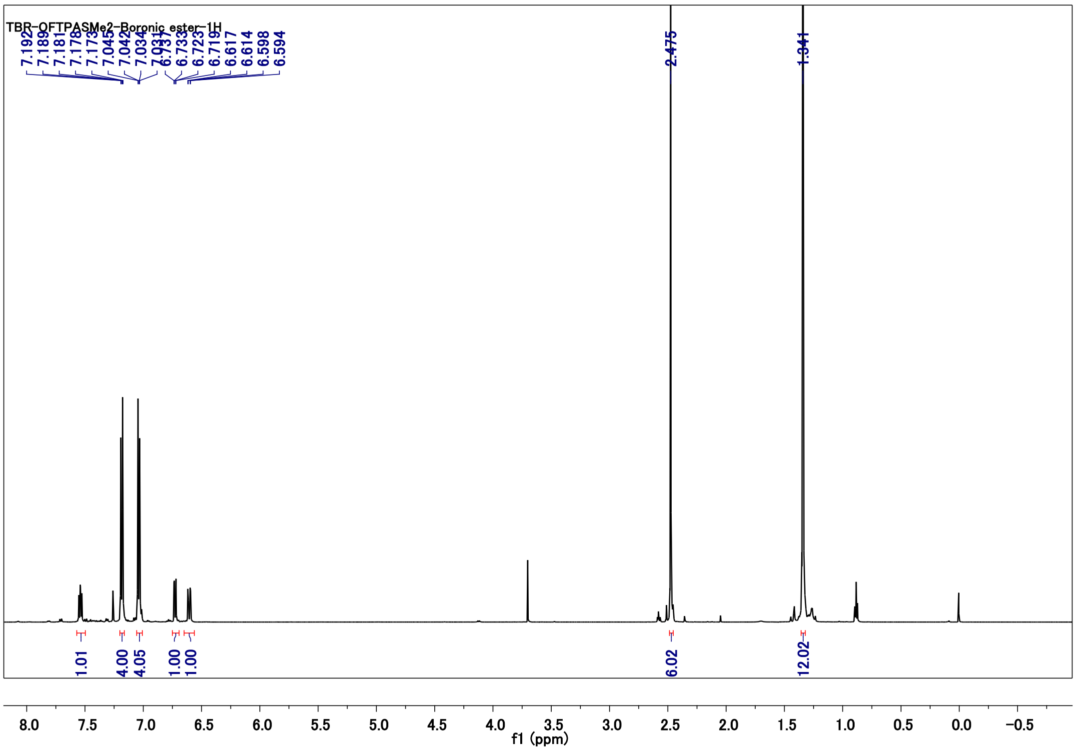


Fig. S4. ^{1}H NMR spectrum of compound 8 in deuterated chloroform.

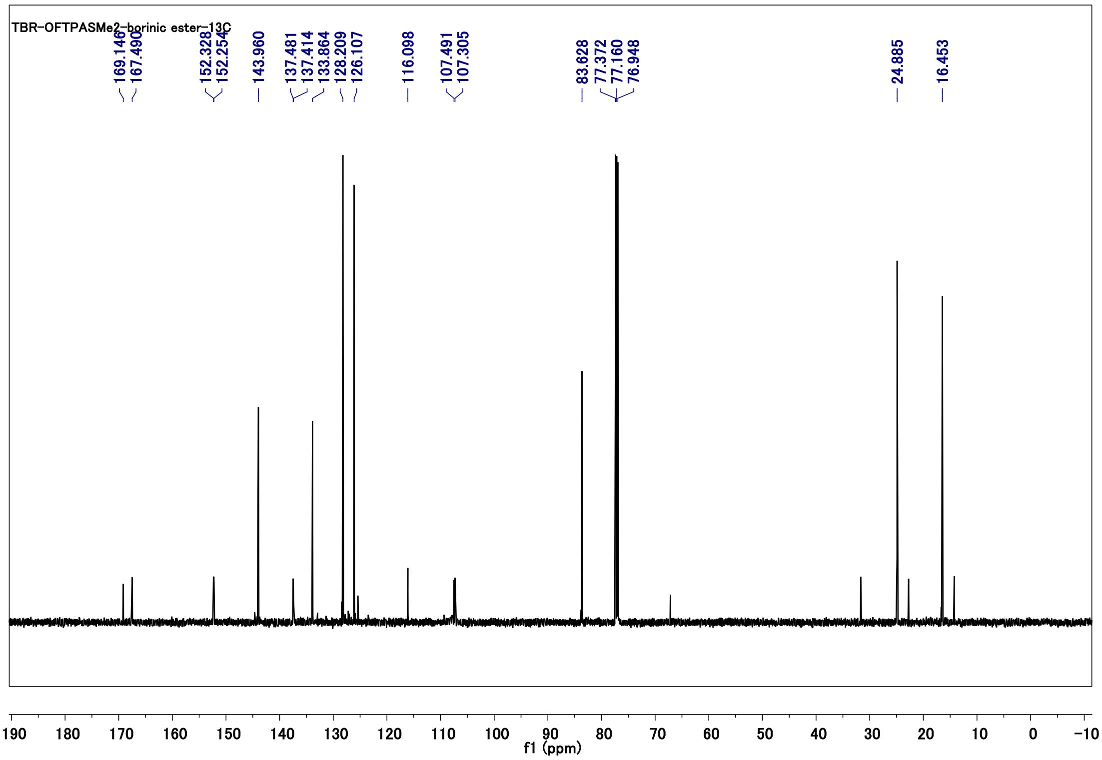


Fig. S5. ^{13}C NMR spectrum of compound 8 in deuterated chloroform.

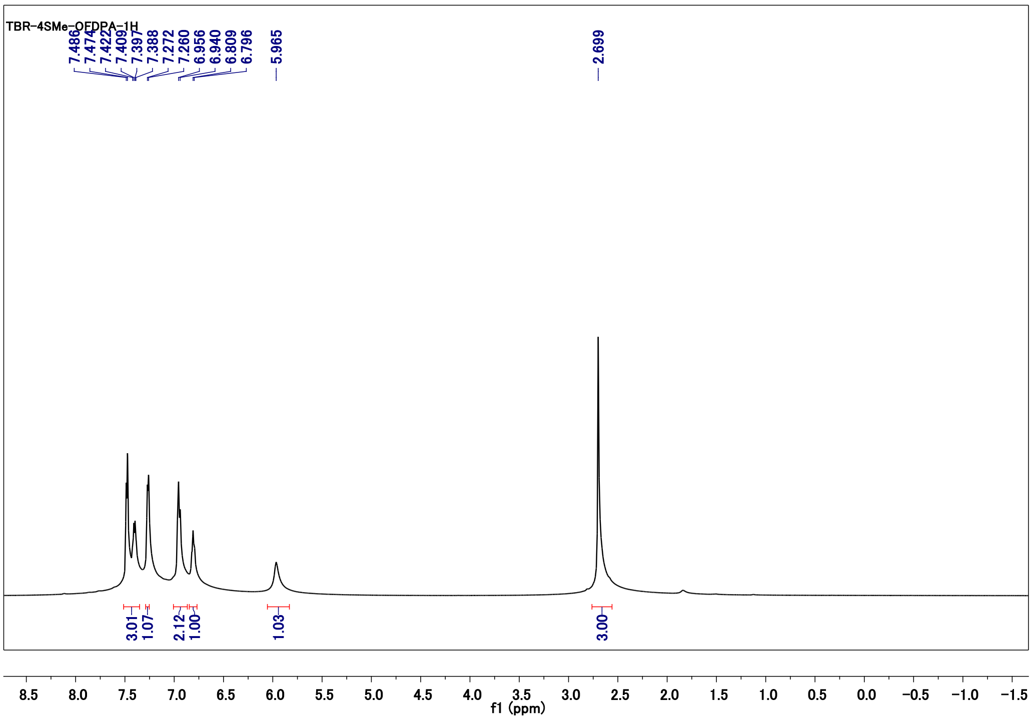


Fig. S6. ^{1}H NMR spectrum of compound **9** in deuterated chloroform.

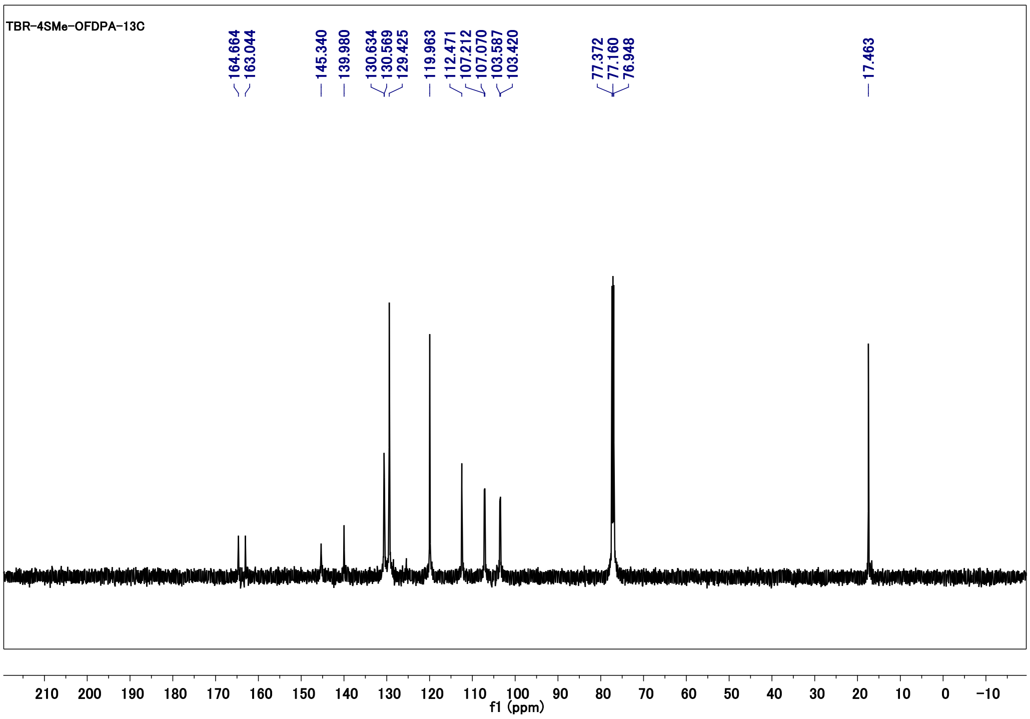


Fig. S7. ^{13}C NMR spectrum of compound **9** in deuterated chloroform.

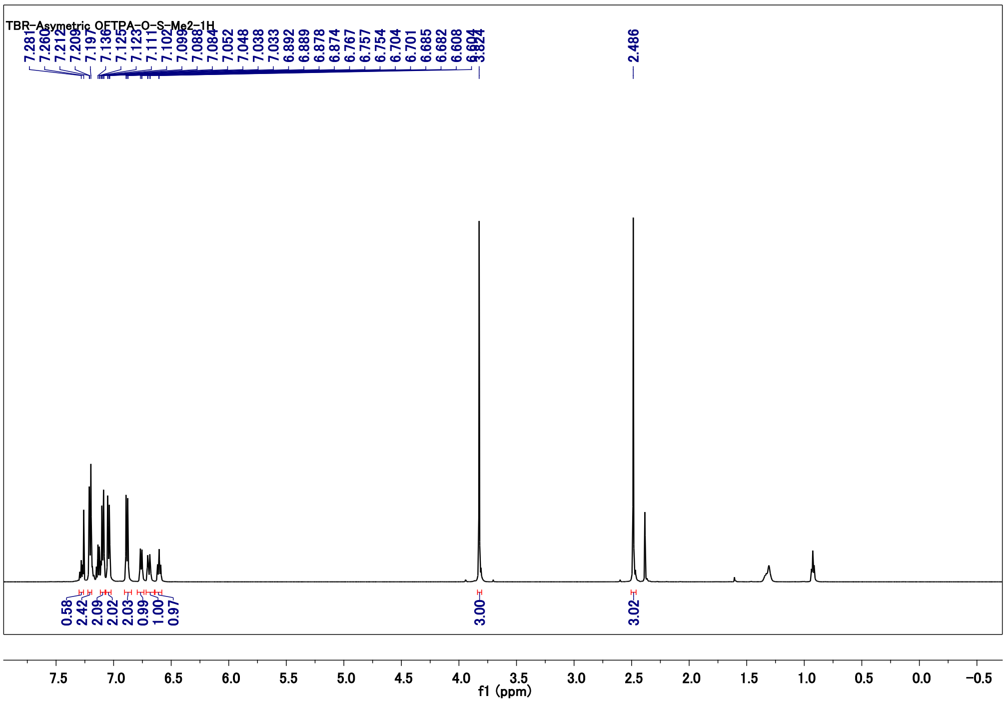


Fig. S8. ^{1}H NMR spectrum of compound **10** in deuterated chloroform.

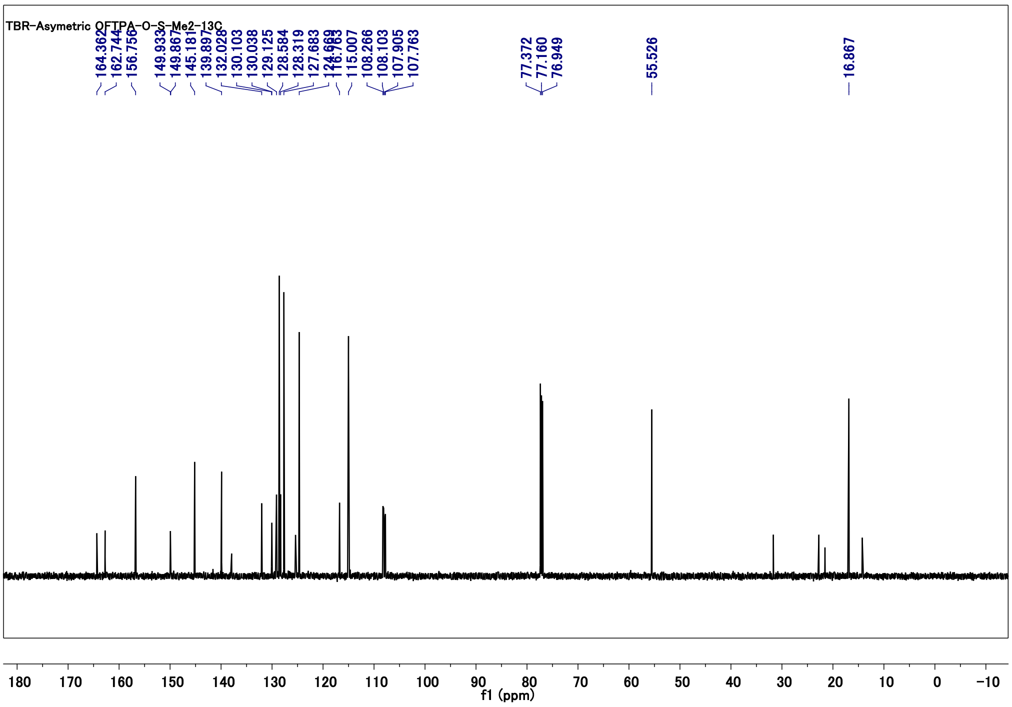


Fig. S9. ^{13}C NMR spectrum of compound **10** in deuterated chloroform.

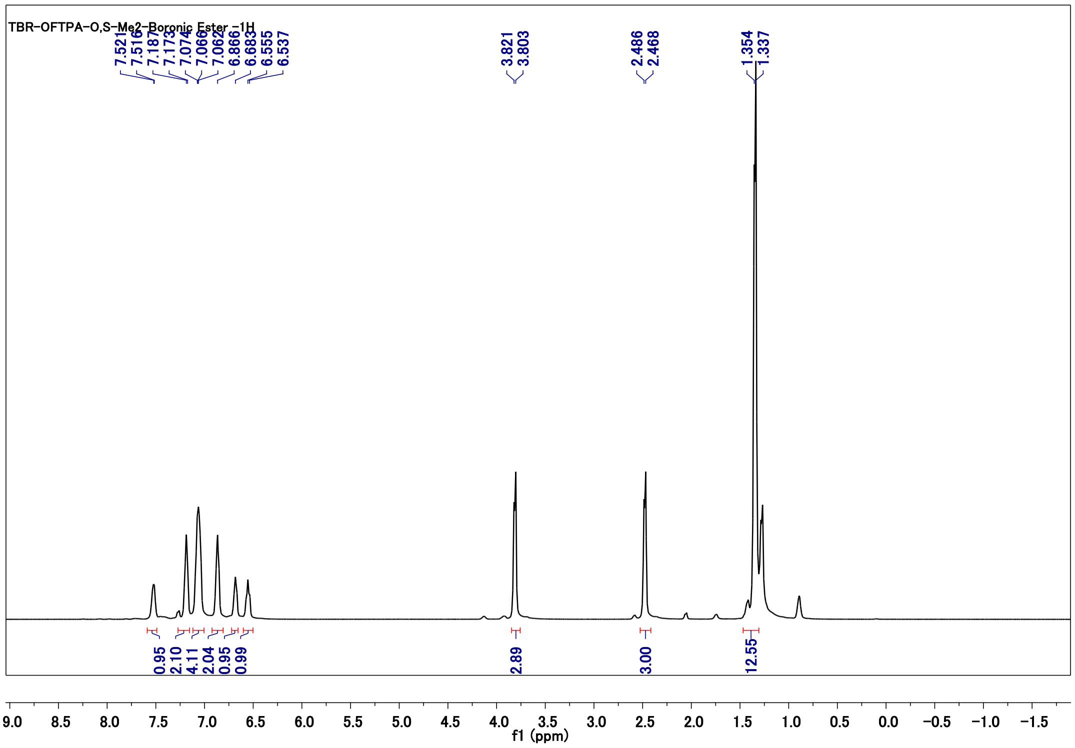


Fig. S10. ^{1}H NMR spectrum of compound **12** in deuterated chloroform.

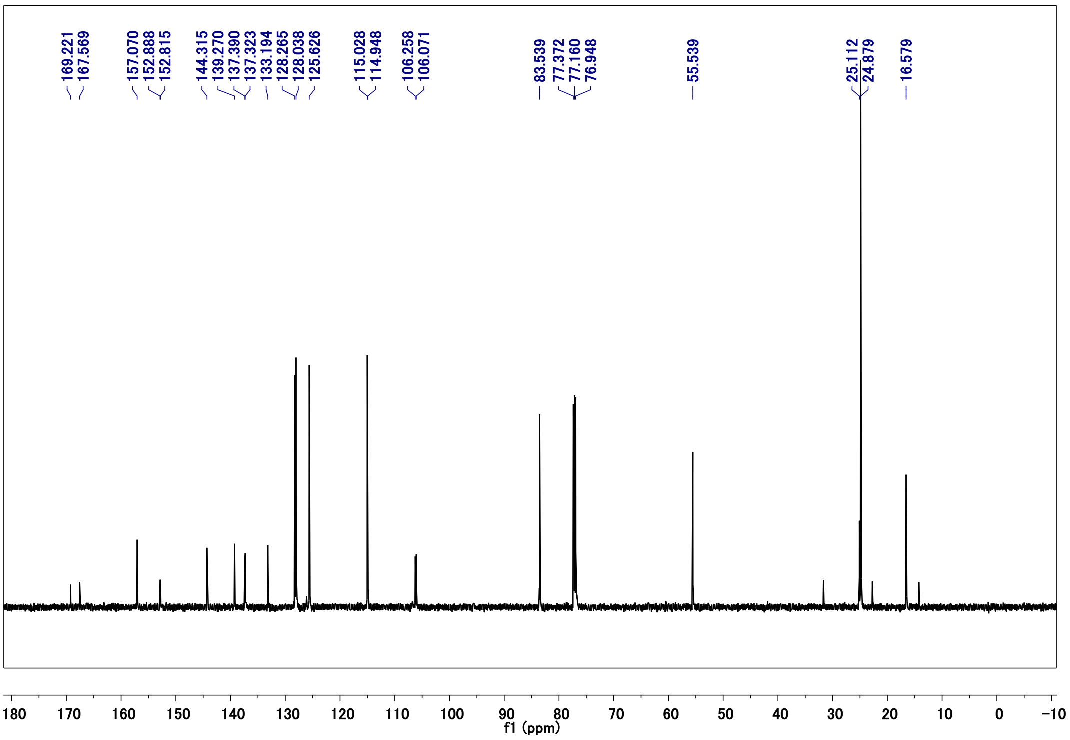


Fig. S11. ^{13}C NMR spectrum of compound 12 in deuterated chloroform.

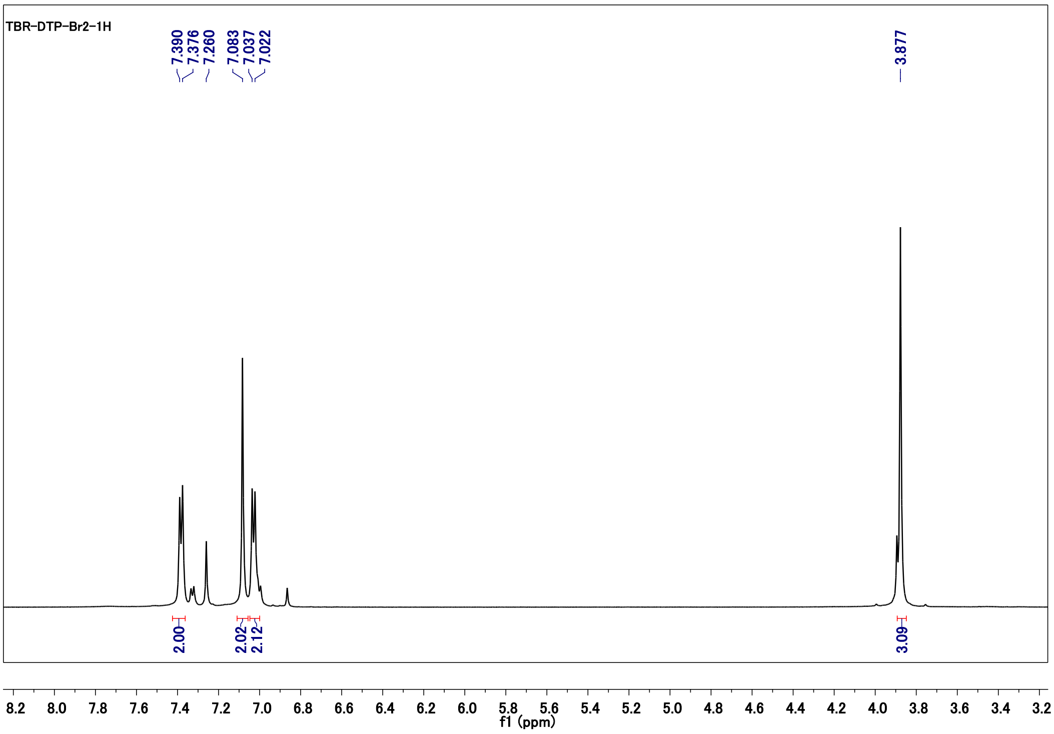


Fig. S12. ^{1}H NMR spectrum of compound **14** in deuterated chloroform.

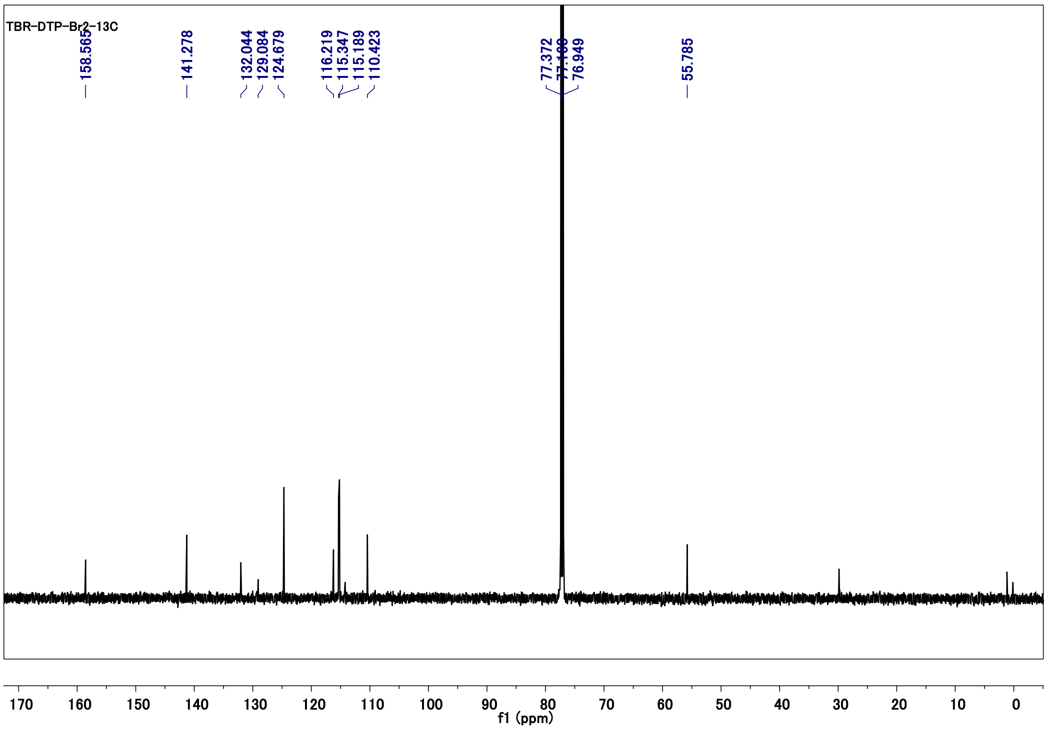


Fig. S13. ^{13}C NMR spectrum of compound 14 in deuterated chloroform.

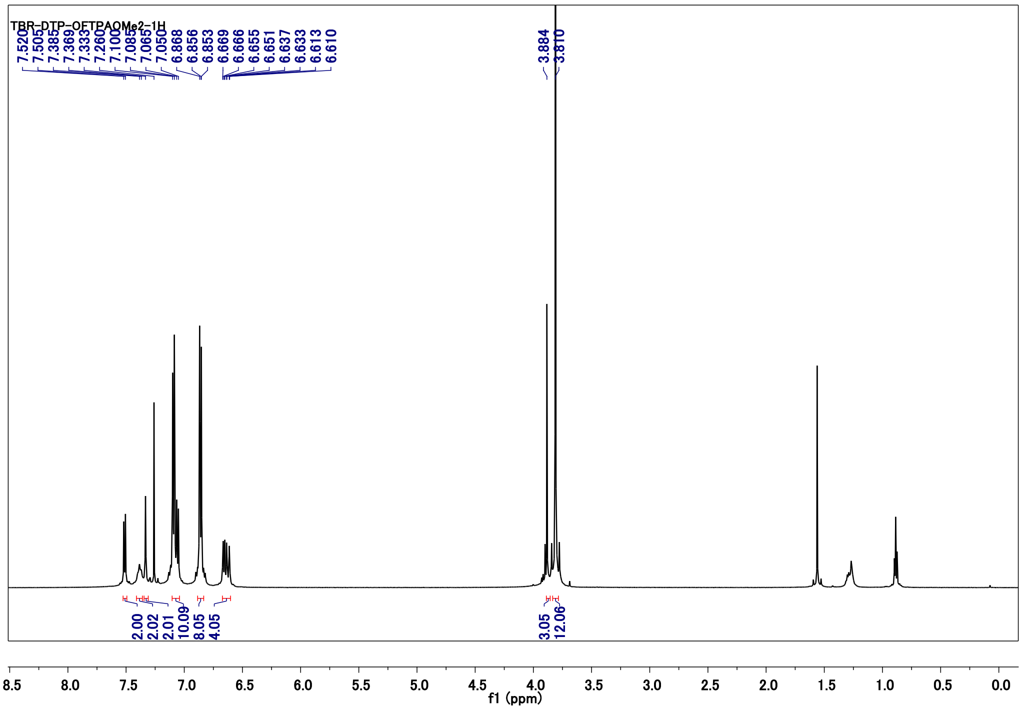


Fig. S14. ^{1}H NMR spectrum of DTP-FO in deuterated chloroform.

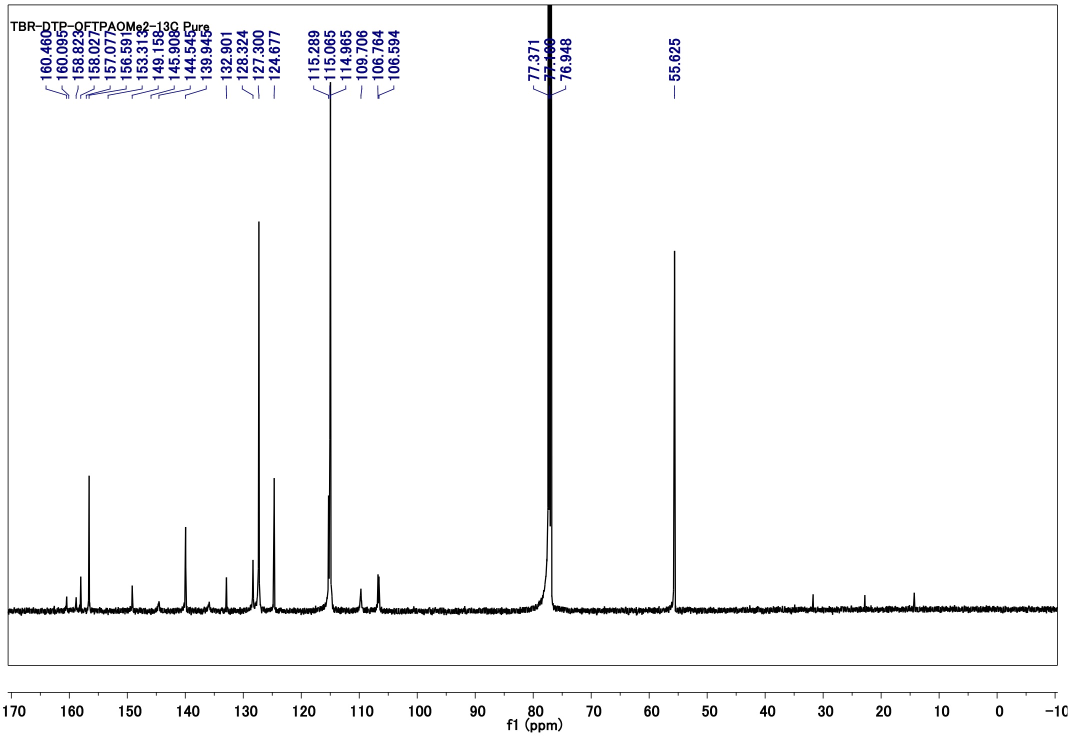


Fig. S15. ^{13}C NMR spectrum of DTP-FO in deuterated chloroform.

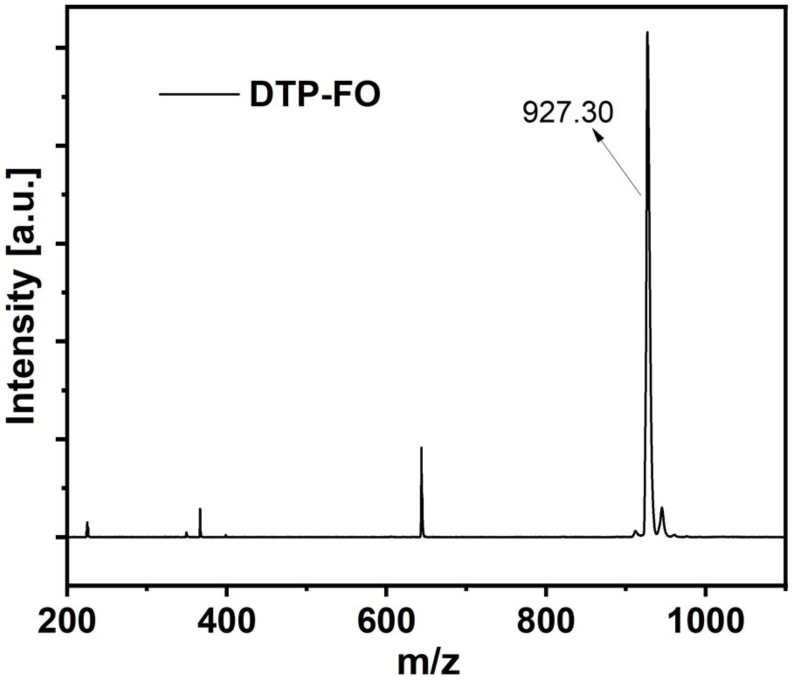


Fig. S16. Mass spectrum of DTP-FO.

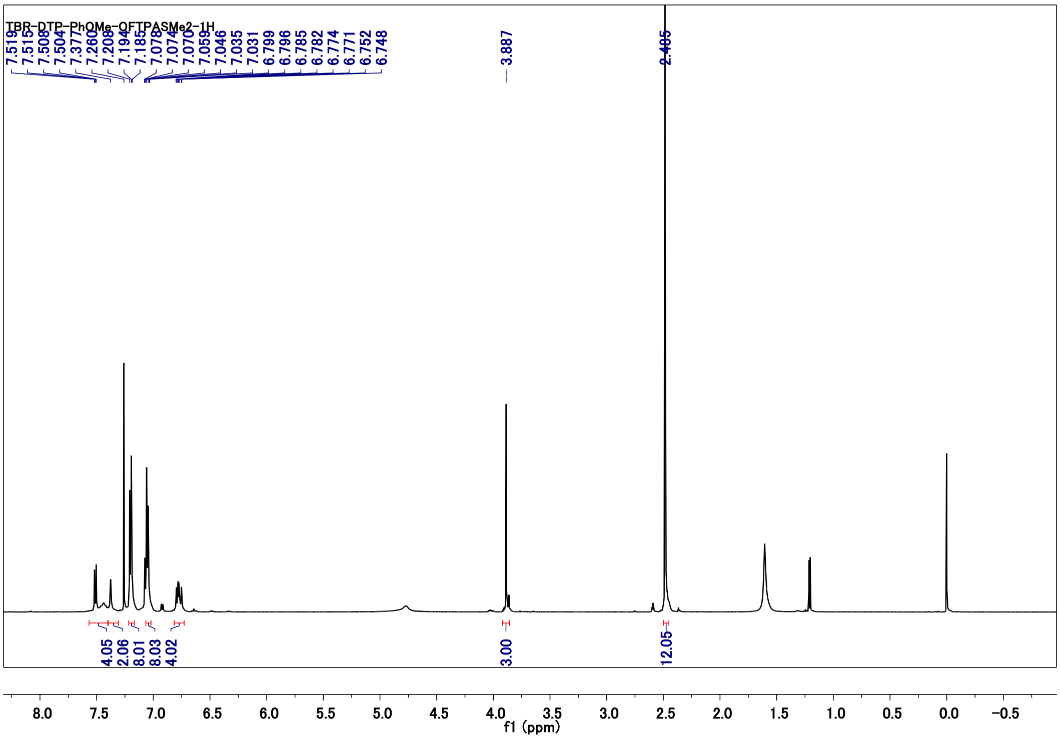


Fig. S17. ^{1}H NMR spectrum of DTP-FS in deuterated chloroform.

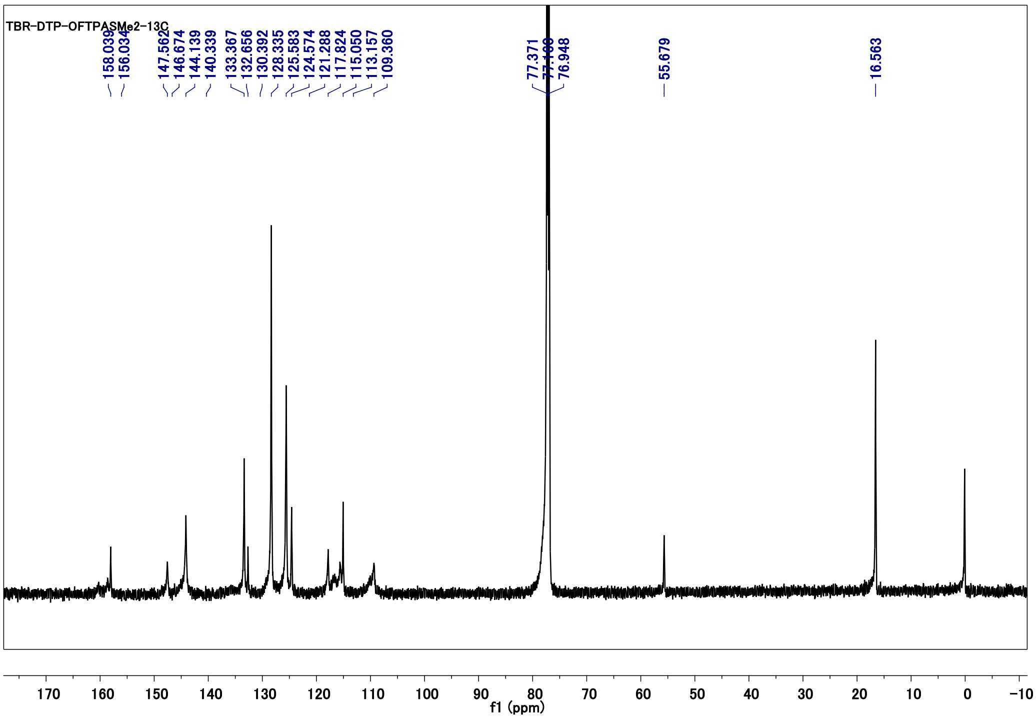


Fig. S18. ^{13}C NMR spectrum of DTP-FS in deuterated chloroform.

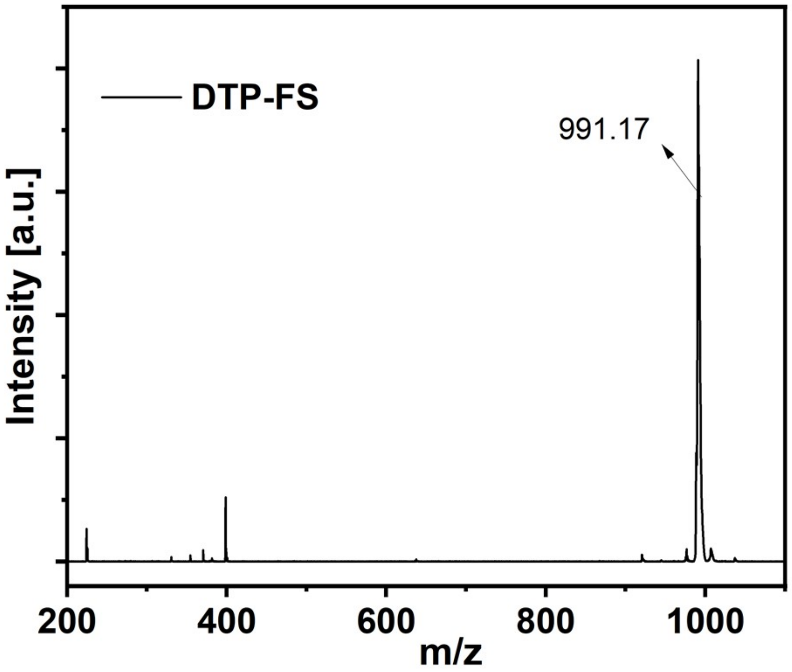


Fig. S19. Mass spectrum of DTP-FS.

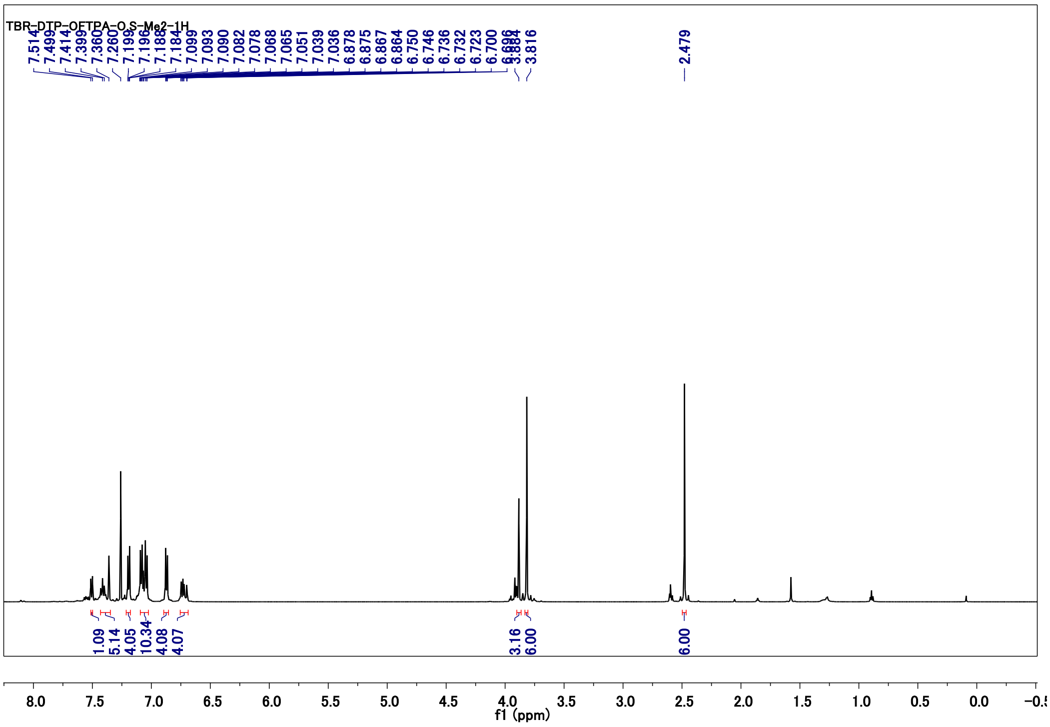


Fig. S20. ^{1}H NMR spectrum of DTP-FOS in deuterated chloroform.

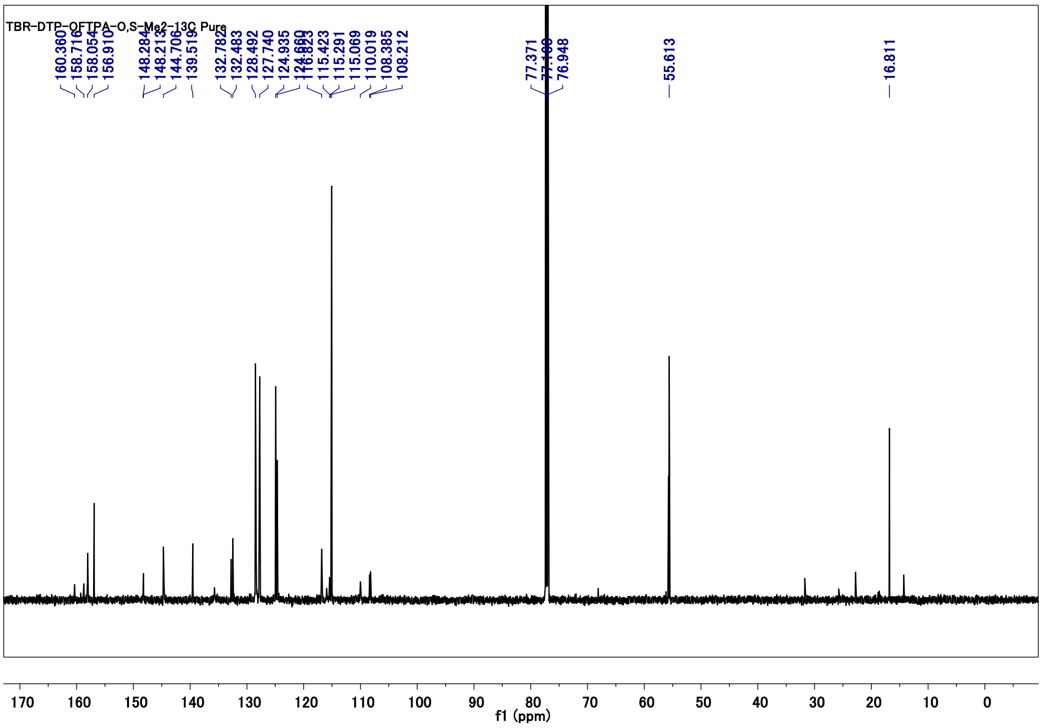


Fig. S21. ^{13}C NMR spectrum of DTP-FOS in deuterated chloroform.

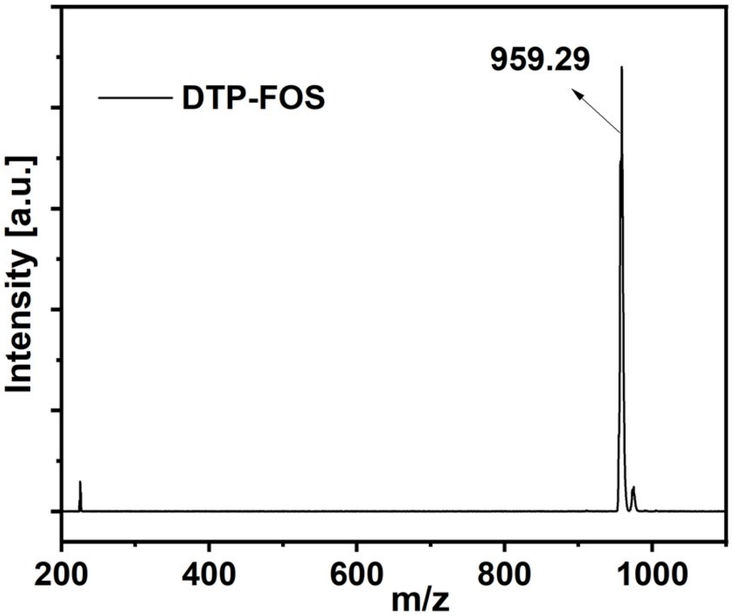


Figure S22. Mass spectrum of DTP-FOS.

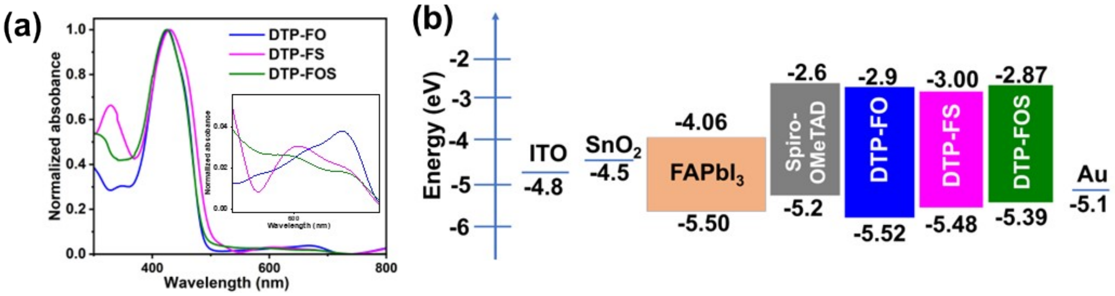


Fig. S23. (a) UV–Vis absorption spectra of doped HTM thin films deposited on fused silica substrates. The inset provides an enlarged view of the long-wavelength region, clearly illustrating the appearance of new absorption features associated with charge-transfer processes. (b) Energy-level diagram of doped HTMs.

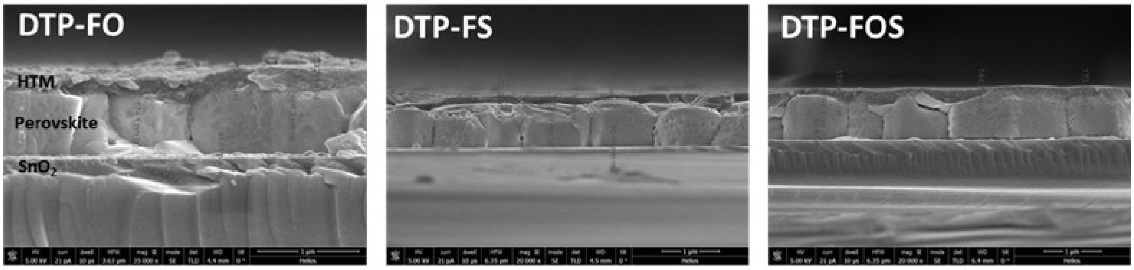


Fig. S24. Cross-sectional SEM images of PSCs. A clear layer structure is observed in all the devices.

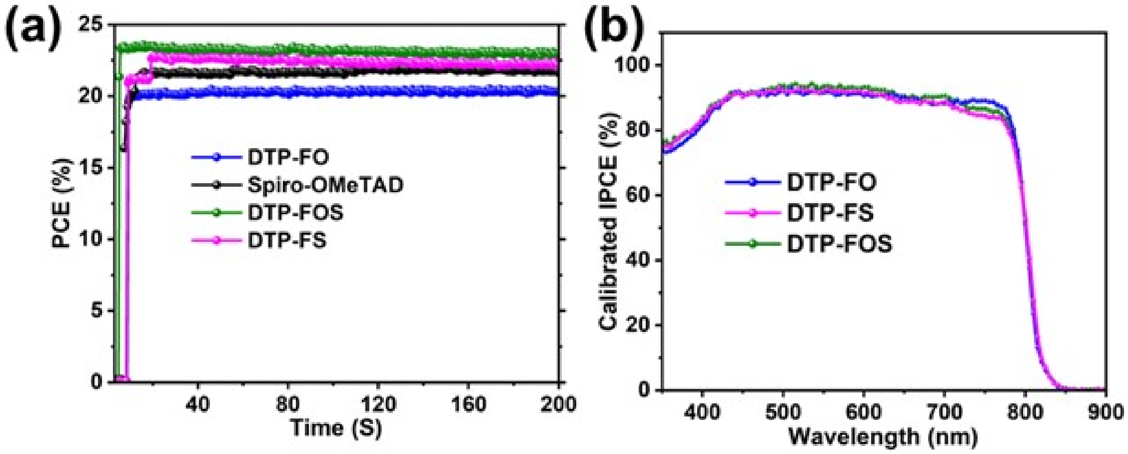


Fig. S25. (a) PCE tracking and (b) EQE spectra of devices with doped HTM layers.

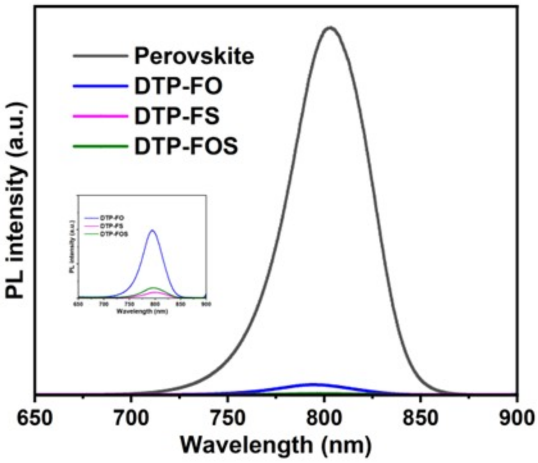


Fig. S26. PL spectra of perovskite films with and without the overlying HTM layers.

Table S1. PL lifetimes of perovskite films with various HTMs.

HTM	τ_1 (ns)	τ_2 (ns)	Average τ
Spiro-OMeTAD	0.05	90	55.45
DTP-FO	0.16	94.1	53.45
DTP-FS	0.09	114	70.64
DTP-FOS	0.11	92.9	62.55

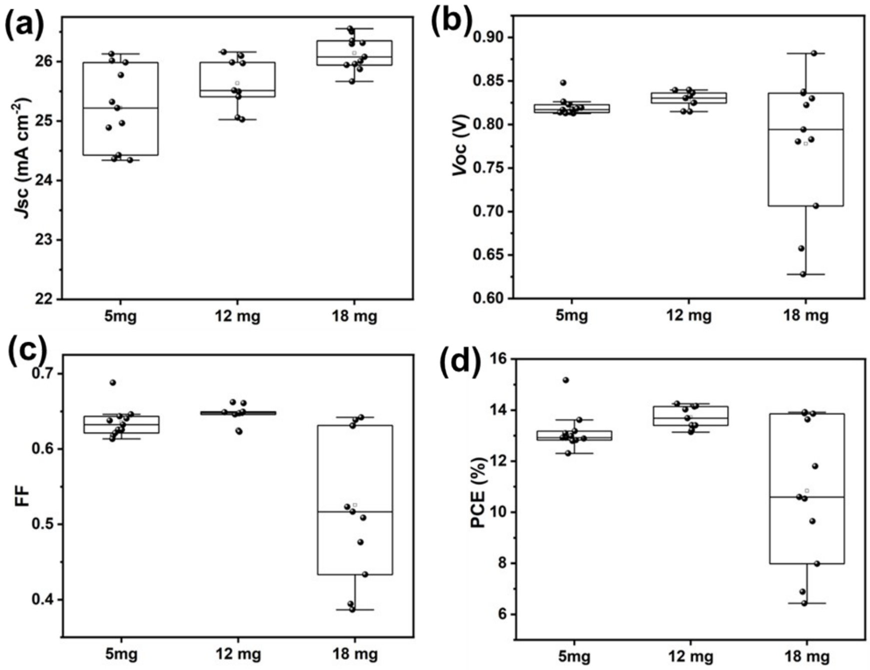


Fig. S27. Plots of (a) J_{sc}, (b) V_{oc}, (c) FF, and (d) PCE for PSCs as a function of the weight concentration (mg mL^{-1}) of the undoped DTP-FOS solutions.

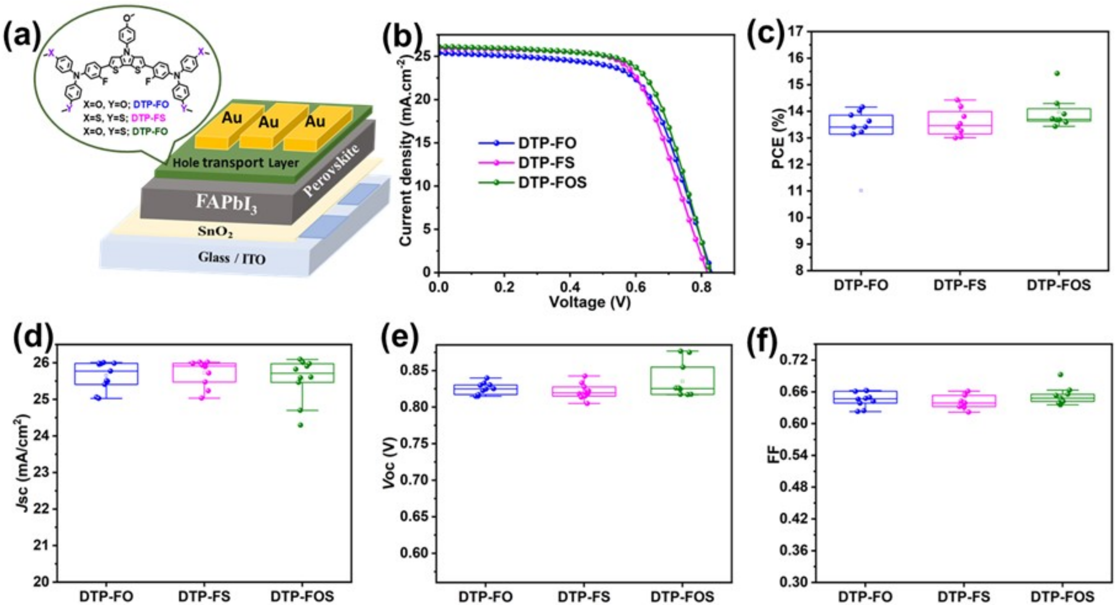
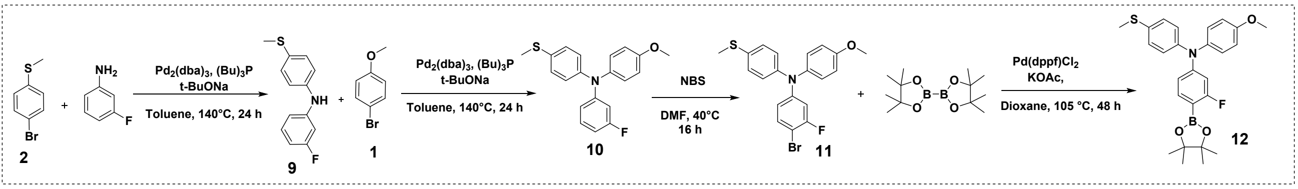


Fig. S28. (a) Schematic illustration of the PSC architecture incorporating undoped HTMs. (b) Representative J–V curves of the undoped devices measured under AM 1.5G illumination at 100 mW cm^{-2}. (c–f) Statistical distributions of the photovoltaic parameters for the as-fabricated PSCs, based on an average of 10 individual devices.

Table S2. Cost evaluation for DTP-FOS synthesis

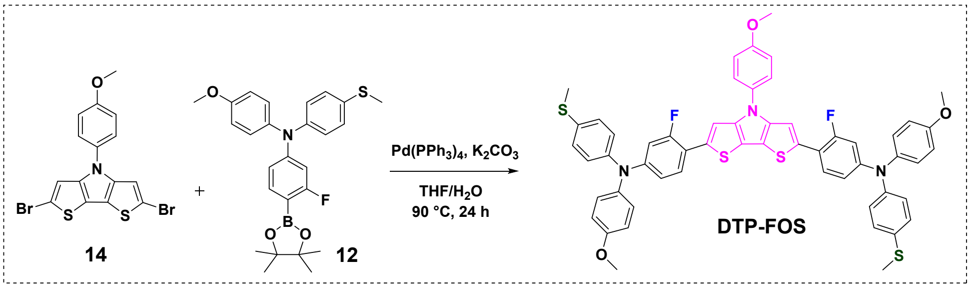


Regent	**Amount / g**	**Amount / mL**	**Price JPY (g or mL)**	**Total Cost** (JPY)	**Target product (JPY/g)**
3-Fluoroaniline	5		5g – 3960 JPY	3960	
4-Bromothioanisole	11.5		25g – 4680 JPY	2152	
t-BuOK	13		100g – 4100 JPY	503	
P(*t*-Bu)$_3$	0.362		5g – 32,900 JPY	2381	
Pd$_2$(dba)$_3$	0.41		5g – 33,210 JPY	2723	
Toluene		80	500 mL – 950 JPY	152	
CHCl$_3$		1800	25 kg –17,700 JPY	1274	
Silica gel	500		25 kg –114,000 JPY	2280	
Hexane		600	15 kg – 6,350 JPY	254	
Total				15679	Produt-9 (1742 JPY /g)
Product-9	5		5g – 8710 JPY	8710	
4-Bromooanisole	11.3		25g – 4680 JPY	2124	
t-BuOK	26		100g – 4100 JPY	1066	
P(*t*-Bu)$_3$	0.362		5g – 32,900 JPY	2381	
Pd$_2$(dba)$_3$	0.41		5g – 33,210 JPY	2723	
Toluene		80	500 mL – 950 JPY	152	
CHCl$_3$		1800	25 kg –17,700 JPY	1274	
Silica gel	500		25 kg –114,000 JPY	2280	
Hexane		600	15 kg – 6,350 JPY	254	
Total				20964	Produt-10 (2329 JPY /g)

3-Fluoro-N-(4-methoxyphenyl)-N-(4-(methylthio)phenyl)aniline (10)	2		1g – 2329 JPY	4658	
NBS	1		100 g – 3030 JPY	30.3	
DMF		25	500 mL – 1760	88	
$CHCl_3$		1800	25 kg – 17,700 JPY	1274	
Silica gel	200		25 kg – 114,000	912	
Hexane		300	15 kg – 6,350 JPY	127	
Total				7089	Produt-11 (2835 円 /g)

Regent	**Amount / g**	**Amount / mL**	**Price JPY (g or mL)**	**Total Cost** (JPY)	**Target product** (JPY /g)
4-Bromo-3-fluoro-N-(4-methoxyphenyl)-N-(4-(methylthio)phenyl)aniline (11)	12		1g – 2835 JPY	34,020	
Bis(pinacolato)diboron	7		25g – 7500 JPY	2,100	
CH_3COOK	13.5		500g – 2430 JPY	66	
Pd(dppf)Cl_2	3		5g – 28100 JPY	16,860	
Dioxane		80	500 – 1760 JPY	281	
$CHCl_3$		1800	25kg –17,700 JPY	1274	
Hexane		600	15 kg – 6,350 JPY	254	
Silica gel	500		25 kg –114,000 JPY	2280	
Total				57,135	Produt-12 (6348 JPY /g)

Table S3. Cost evaluation for DTP-FOS synthesis



Regent	Amount / g	Amount / mL	Price JPY (g or mL)	Total Cost (JPY)	Target product (JPY /g)
2,6-Dibromo-4-(4-methoxyphenyl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole (14)	0.2		1g – 2343 JPY	468	
3-Fluoro-*N*-(4-methoxyphenyl)-*N*-(4-(methylthio)phenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (12)	0.5		1g – 6348 JPY	3174	
$Pd(PPh_3)_4$	0.03		5g – 16,300 JPY	97.8	
THF		25	500 mL – 2050 JPY	102.5	
$CHCl_3$		1800	25 kg – 17,700 JPY	1274	
Silica gel	300		25 kg – 114,000 JPY	1368	
Total				6484	Produt-14 **(20262** JPY **/g)**

However, several important parameters (e.g. energy consumption, waste treatment and labor), it was multiplied by a factor of 1.5 to get a more realistic estimation of lab synthesis costs of ~50,655 JPY/g. This is less than the costs of purified spiro-OMeTAD (~66,500 JPY/g, high purity,Ossila).

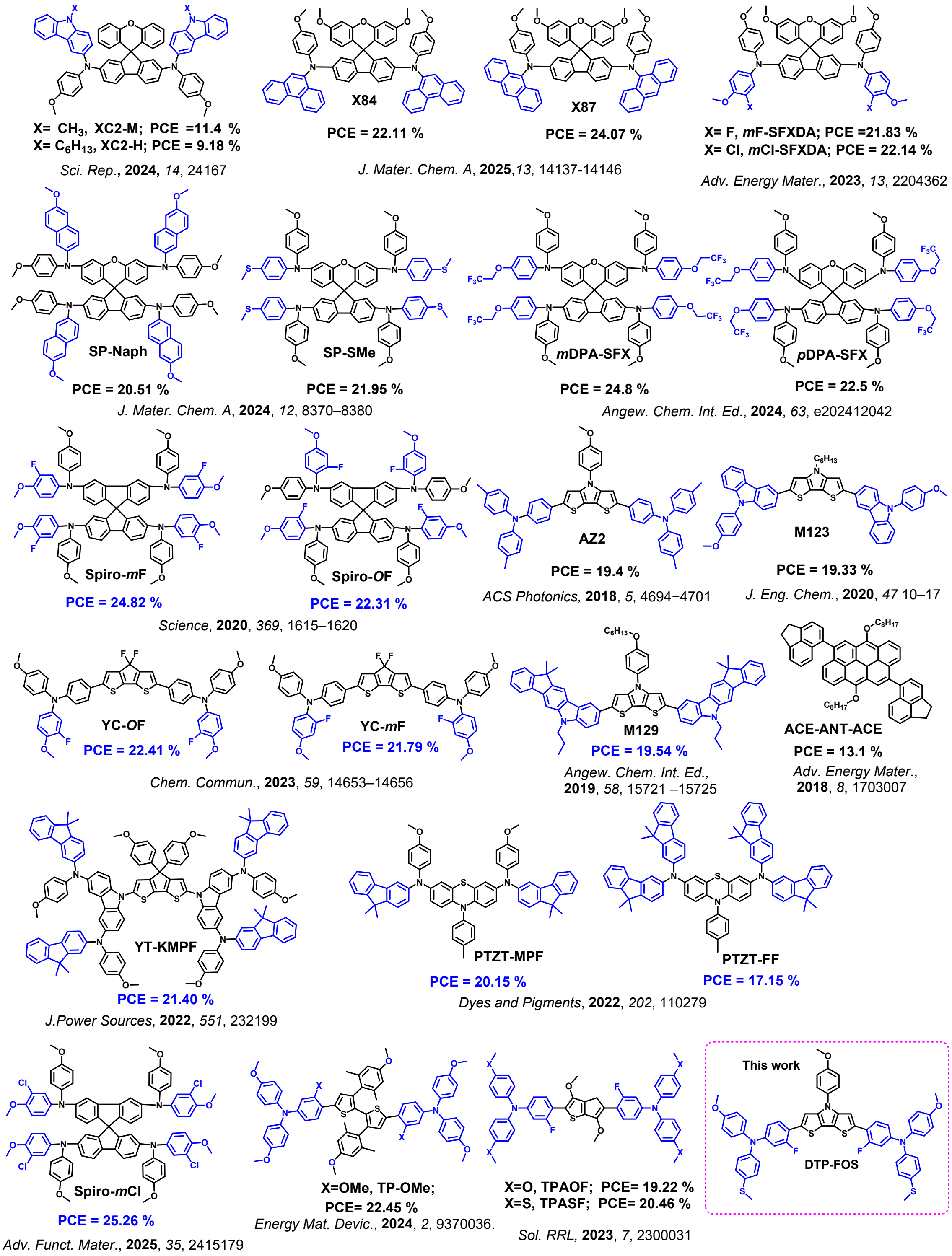


Fig. S29. Summary of reported HTMs with various terminal groups.

References:

S1. M. Zhai, N. Shibayama, T. B. Raju, T. Wu, C. Chen, Z. Guo, T. Matsushima, T. Miyasaka and M. Cheng, *Small* **2025**, 2505961.

S2. T. B. Raju, C. A. M. Senevirathne, M. Watanabe, Y. Fujita, D. Senba and T. Matsushima, *J. Mater. Chem. C,* 2025,**13**, 15082-15090.

S3. S. Mabrouk, M. Zhang, Z. Wang, M. Liang, B. Bahrami, Y. Wu, J. Wu, Q. Qiao and S. Yang, *J. Mater. Chem. A*, 2018, **6**, 7950–7958.

S4. J. Manit, P. Kanjanaboos, P. Naweephattana, A. Naikaew, L. Srathongsian, C. Seriwattanachai, R. Supruangnet, H. Nakajima, U. Eiamprasert and S. Kiatisevi, *Sci Rep.*, 2024, **14,** 24167.

S5. D. Zhang, Q. Long, B. Sun, X. Luo, G. Zhou, J. Huang, Z. Zhang, J. Su and B. Xu, *J. Mater. Chem. A,* 2025, **13**, 14137–14146.

S6. V. Kumar, D. Kumar, R. D. Chavan, K. P. Kumar, B. Yadagiri, M. Ans, J. Kruszyńska, A. Mahapatra, J. Nawrocki, K. Nikiforow, N. Mrkyvkova, P. Siffalovic, P. Yadav, S. Akin, S. P. Singh and D. Prochowicz, *J. Mater. Chem. A*, 2024, **12**, 8370–8380.

S7. X. Ding, X. Zhou, H. Wang, M. Zhai, Z. Xia, L. Liu, Y. Tian, C. Chen and M. Cheng, *New J. Chem.*, 2023, **47**, 16666–16674.

S8. Z. Zhang, C. Duan, S. Wang, T. Xie, F. Zou, Y. Luo, R. Tang, K. Guo, L. Yuan, K. Zhang, Y. Wang, J. Qiu and K. Yan, *Angew. Chem. Int. Ed.,* 2024, **63**, e202412042

S9. H. Zhang, X. Yu, M. Li, Z. Zhang, Z. Song, X. Zong, G. Duan, W. Zhang, C. Chen, W. H. Zhang, Y. Liu and M. Liang, *Angew. Chem. Int. Ed.,* 2023, **62**, e202314270.

S10. X. Zhang, S. Zhang, X. Liao, B. Ding, G. Rahim, K. Zhao, J. Chen, M. Han, Y. Zhou, P. Shi, K. Zhang, S. Kinge, H. Zhang, R. Wang, K. G. Brooks, S. Dai, X. Liu, Z. Fei, P. J. Dyson, M. K. Nazeeruddin and Y. Ding, *Adv. Funct. Mater.,* 2024, **34**, 2314086.

S11. X. Liu, X. Zhang, Y. Zhou, W. Dai, J. Chen, O. A. Syzgantseva, M. A. Syzgantseva, B. Li, R. Ghadari, M. Han, W. Du, Z. Shao, Q. Wang, S. Dai, M. K. Nazeeruddin and Y. Ding, *Adv. Funct. Mater.*, 2025, **35**, 2415179.