# **Supporting Information**

# Effect of *Ortho*-Fluorine Substituted Hole Transport Materials for Perovskite Solar Cells: Influence of Rigid vs. Flexible Linkers

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### 1. Experimental section

#### **1.1.** Materials and methods.

All solvents and chemicals were purchased from Aldrich 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

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE III 600 MHz spectrometer in deuterated chloroform (CDCl<sub>3</sub>), using tetramethylsilane (TMS) as an internal standard. Chemical shifts were referenced to the deuterated solvent (CDCl<sub>3</sub>:  $\delta = 7.26$  ppm for <sup>1</sup>H and  $\delta =$ 77.23 ppm for <sup>13</sup>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 S8-S26. UV-VIS-NIR absorption spectra were measured for both solution-state (chloroform) and thin-film samples (fabricated on quartz substrates) using a Jasco V-730 spectrophotometer. Fluorescence spectra of the same samples were recorded on a Jasco FP-8300 fluorescence spectrophotometer. Photoelectron yield spectroscopy (PYS; AC-2, Rikenkeiki) was performed on HTM layers. Single-crystal X-ray diffraction (SCXRD) data for DTP-OFTPASMe2 were collected using a Rigaku SCX-mini diffractometer at 293(2) K. The ground-state geometries and vertical excitation energies of the synthesized HTM molecules were studied computationally using density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations, employing the B3LYP functional with a 6-31G(d,p) basis set in the Gaussian 16 software package.

### 1.3. Synthetic procedure

All reagents and chemicals, including compounds **1** and **2**, as well as 2,6-dibromo-4*H*-cyclopenta[2,1-*b*:3,4-*b*']dithiophen-4-one (**6**), 3,3'-dibromo-2,2'-bithiophene, and dithieno[3,2-b:2',3'-d]thiophene, were commercially purchased and used without further purification. Solvents were purified using standard methods and dried when necessary. The starting materials and HTMs, including 2,6-dibromodithieno[3,2-*b*:2',3'-*d*]thiophene (**9**), 5,5'-dibromo-3,3'-

diethoxy-2,2'-bithiophene (10), and 2,6-dibromo-4-(4-methoxyphenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (11), were synthesized according to previously reported methods.<sup>[S1-S7]</sup>



### (a) Synthesis of starting materials

### (b) Synthesis of HTMs:



Figure S1. Synthetic routes of the four HTMs.

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

A solution of 3-fluoroaniline (5 g, 44.9 mmol), 4-bromothioanisole (22.70 g, 112.5 mmol), t-BuONa (25.9 g, 269 mmol), and P(t-Bu)<sub>3</sub> (0.362 g, 1.8 mmol) in dry toluene (80 mL) was degassed under nitrogen for 30 minutes.  $Pd_2(dba)_3$  (411 mg, 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 light green liquid and purified by column chromatography (hexane/chloroform, 3:1, v/v). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) 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-3-fluoro-N,N-bis(4-(methylthio)phenyl)aniline (4)

To a solution of compound **3** (20 g, 56.26 mmol) in *N*,*N*-dimethylformamide (DMF) (30 mL), *N*-bromosuccinimide (NBS) (11 g, 61.79 mmol) was added at 0°C. The reaction mixture was stirred at 0°C for 15 minutes in the dark, then gradually warmed to 40°C and stirred for an additional 24 hours. Upon completion of the reaction, the crude product was quenched with water and extracted with chloroform. The residue was purified by column chromatography (hexane/chloroform, 3:1, v/v), affording compound **4** as a pale green viscous oil (0.85 g, 75%).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) 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). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) 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-(methylthio)phenyl)-4-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)aniline (5)

Compound **4** (12 g, 27.62 mmol) and bis(pinacolato)diborane (7 g, 27.62 mmol) were dissolved in dry dioxane along with potassium acetate (13.5 g, 138 mmol) and Pd(dppf)Cl<sub>2</sub> (3 g, 4.1 mmol). Under a nitrogen atmosphere, the mixture was heated to 110°C and stirred overnight. The reaction mixture was then extracted with chloroform, washed with water, and purified by column chromatography (hexane/chloroform, 2:1, v/v), affording compound **5** as an orange-red solid (0.68 g, 72%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  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.

#### **General synthesis of HTMs**

Suzuki reaction (7 and 12–14): Organo boronate (5, 2.5 eq), bromide (9–11, 1 eq), 2 M  $K_2CO_3$  (aq), and Pd(PPh<sub>3</sub>)<sub>4</sub> (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<sub>4</sub>, and the solvent was removed via rotary evaporation. The crude product was purified by silica gel column chromatography.

### Synthesis of 2,6-bis(4-(bis(4-(methylthio)phenyl)amino)-2-fluorophenyl)-4Hcyclopenta[2,1-b:3,4-b']dithiophen-4-one (7)

Compound 7 was also synthesized via a Suzuki reaction and purified by column chromatography using chloroform, yielding a 69% product. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 (t, J = 8.6 Hz, 1H), 7.20 (d, J = 8.0 Hz, 5H), 7.04 (d, J = 8.3 Hz, 4H), 6.74 (dd, J = 16.7, 11.4 Hz, 2H), 2.48 (s, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  183.48, 160.16, 158.51, 148.52, 148.10, 143.90, 142.04, 140.36, 133.94, 128.36, 127.92, 125.91, 118.72, 117.38, 114.66, 108.74, 77.3, 77.16, 76.95, 68.10, 25.73, 25.48, 16.53.

### Synthesis of 2-(2,6-bis(4-(bis(4-(methylthio)phenyl)amino)-2-fluorophenyl)-4Hcyclopenta[2,1-b:3,4-b']dithiophen-4-ylidene)malononitrile (CPDT-OFTPASMe2) (8)

Compound 7 (1 mmol) and malononitrile (3.06 mmol) were dissolved in dry THF and acetic acid (9:1). A catalytic amount of pyridine was then added to the reaction mixture under a nitrogen atmosphere. The mixture was heated to 85°C and stirred overnight. After completion, the crude product was extracted with chloroform, washed with water, and purified by column chromatography using chloroform as the eluent to afford compound CPDT-OFTPASMe2 (8) as a blackish-green solid (85%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 (s, 1H), 7.33 (t, J = 8.7 Hz, 1H), 7.23 – 7.18 (m, 4H), 7.07 – 7.01 (m, 4H), 6.74 (dd, J = 15.7, 11.1, 2.3 Hz, 2H), 2.49 (s, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  160.09, 158.44, 154.26, 148.73, 144.33, 143.61, 140.96, 140.70, 134.20, 128.26, 127.68, 126.03, 119.49, 116.92, 113.66, 112.55, 108.14, 77.37, 77.16, 76.95, 16.42.

### Synthesis of 4,4'-(dithieno[3,2-b:2',3'-d]thiophene-2,6-diyl)bis(3-fluoro-N,N-bis(4-(methylthio)phenyl)aniline) (TTT-OFTPASMe2) (12)

Compound TTT-OFTPASMe2 (12) was synthesized via a Suzuki reaction and subsequently purified by column chromatography, yielding a yellow solid with a 72% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.55 (s, 1H), 7.42 (d, J = 8.7 Hz, 1H), 7.21 (d, J = 8.6 Hz, 4H), 7.06 (d, J = 8.6 Hz, 4H), 6.82 – 6.75 (m, 2H), 2.49 (s, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  160.50, 158.84,

148.31, 144.05, 141.88, 138.24, 133.73, 129.97, 128.61, 128.37, 125.83, 118.61, 117.60, 115.59, 109.17, 109.00, 77.37, 77.16, 76.95, 16.57.

### Synthesis of 4,4'-(3,3'-diethoxy-[2,2'-bithiophene]-5,5'-diyl)bis(3-fluoro-N,N-bis(4-(methylthio)phenyl)aniline) (ThOEt-OFTPASMe2) (13)

Compound ThOEt-OFTPASMe2 (13) was synthesized via a Suzuki reaction and subsequently purified by column chromatography using chloroform, yielding a yellow solid with a 75% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.20 (t, J = 10.6 Hz, 5H), 7.08 – 7.01 (m, 4H), 6.81 – 6.74 (m, 2H), 2.49 (s, 6H), 1.57 (s, 3H), 1.50 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  145.01 – 144.66, 144.66 – 144.13, 133.35, 128.36, 125.58, 117.82, 77.37, 77.16, 76.95, 67.91, 31.69, 22.76, 16.61, 15.42, 14.25.

### Synthesis of 4,4'-(4-(4-methoxyphenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole-2,6-diyl)bis(3fluoro-N,N-bis(4-(methylthio)phenyl)aniline) (DTP-OFTPASMe2) (14)

Compound DTP-OFTPASMe2 (14) was synthesized via a Suzuki reaction and subsequently purified by column chromatography using chloroform, yielding a blackish-green solid with a 72% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  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.

### 2. Device Fabrication

#### 2.1 Materials

The SnO<sub>2</sub> colloidal solution (15% in H<sub>2</sub>O colloidal dispersion) was purchased from Alfa Aesar. FAI, MABr, PbI<sub>2</sub>, PbBr<sub>2</sub>, and CsI were obtained from Tokyo Chemical Industry. Chlorobenzene (CB), 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 sourced from Atsugi Micro.

#### 2.2 Preparation of precursor solutions:

A perovskite precursor solution was prepared by mixing 1.10 M FAI, 0.2 M MABr, 1.15 M PbI<sub>2</sub>, and 0.2 M PbBr<sub>2</sub> in an anhydrous DMF/DMSO solvent mixture (4:1 volume ratio).

Additionally, a 0.08 M CsI solution in DMSO was added to the precursor solution. The resulting solution was stirred at 70°C for 1 hour and then filtered through a 0.2  $\mu$ m polytetrafluoroethylene (PTFE) filter before use. Solutions of the hole transport materials (HTMs) were prepared by dissolving 30 mg of HTM in 0.5 mL CB. This solution was then mixed with 9  $\mu$ L of a LiTFSI solution (520 mg mL<sup>-1</sup> in acetonitrile), 14.5  $\mu$ L of an FK-209 solution (300 mg mL<sup>-1</sup> in acetonitrile), and 15  $\mu$ L of 4-tBP. The HTL precursor solution was also filtered through a 0.2  $\mu$ m PTFE filter before use.

#### **2.3 Fabrication of the devices:**

Glass substrates with a pre-patterned ITO layer (~150 nm thick, Atsugi Micro) and a sheet resistance of ~10  $\Omega$  sq<sup>-1</sup> were sequentially cleaned using ultrasonication in detergent, pure water, acetone, and isopropanol for 10 minutes each. Prior to use, the cleaned ITO-coated substrates underwent UV-ozone treatment for 15 minutes. A thin layer of SnO<sub>2</sub> nanoparticles (SnO<sub>2</sub> colloid solution diluted with pure water at a 1:3 volume ratio) was then spin-coated onto the ITO surfaces at 3,000 rpm for 30 seconds (cell area: 0.04 cm<sup>2</sup>), followed by annealing at 150°C for 30 minutes. After cooling to room temperature, the SnO<sub>2</sub>-coated substrates were subjected to an additional 15-minute UV-ozone treatment. Surface treatment was carried out using a 0.1 mM KOH solution in water, which was spin-coated at 3,000 rpm for 30 seconds, followed by annealing at 100°C for 10 minutes. The perovskite layer was deposited using a two-step spin-coating process: 1,000 rpm for 10 seconds, followed by 6,000 rpm for 30 seconds. Ten seconds before the completion of spin-coating, 140 µL of CB was dropped onto the spinning substrate. The substrate was then immediately transferred to a hot plate and annealed at 100°C for 30 minutes. Next, the spiro-OMeTAD or synthesized HTM layer was spin-coated onto the perovskite layer at 4,000 rpm for 30 seconds and 3,000 rpm for 30 seconds, respectively. Finally, an ~80-nm-thick Au electrode was thermally deposited under vacuum at a base pressure of  $10^{-4}$  Pa, with a deposition rate of ~0.1 nm s<sup>-1</sup>.

### 2.4 Solar cell performance measurement

All the J-V curves were recorded using a computer-controlled Keysight B2901A source meter under simulated 1-sun illumination generated by a Xe lamp-based solar simulator (HAL-320, Asahi Spectra), and the scan rate was kept at 0.01 V s<sup>-1</sup>. The illumination intensity of the light source was accurately calibrated by using a standard Si photodiode detector that was certificated by the National Institute of Advanced Industrial Science and Technology (AIST, Japan). The original PSC area, defined by the overlap of the ITO and Au electrodes, was 0.04 cm<sup>2</sup>, whereas the illumination area during J-V measurements was precisely set to 0.0369 cm<sup>2</sup> (determined via optical microscopy) using a black shadow mask. The lamp power was carefully calibrated to 100 mW cm<sup>-2</sup> using a crystalline Si reference cell with an amorphous Si optical filter (Bunko-Keiki), certified by the National Institute of Advanced Industrial Science and Technology of Japan. For operational stability evaluation, J-V curves of encapsulated PSCs were periodically measured under continuous white LED illumination at 100 mW cm<sup>-2</sup> (PAS-100, System Engineers). Between J-V scans, the PSCs were held at their maximum power point.



**Figure S2.** Calculated frontier molecular orbitals of the HTMs, illustrating the HOMOs and LUMOs.

**Table S1.** Selected transition wavelengths, oscillator strengths (f), and wave functions of the HTMs, calculated using time-dependent density functional theory (TD-DFT) with the B3LYP functional and the 6-31G(d,p) basis set.

HTM	$\lambda$ (nm)	f	Wave function
	429	1.9875	H → L+1 (97.41%)
CPDT-	565	0.0343	H−2 → L (93.13%)
OFTPASMe2	1021	0.1120	H → L (96.44)
	315	0.1808	H−1 →L+1 (97.62%)
	338	0.0707	H -2 → L (95.33%)
TTT- OFTPASMe2	346	0.0808	H → L+2 (61.50%),
			H → L+3 (29.69%)
	459	2.2076	H → L (97.85%)
	323	0.0202	H → L+6 (91.30%)
ThOEt-	351	0.0867	H −2 → L (92.22%)
OFTPASMe2	387	0.0330	H → L+3 (100%)
	499	2.1490	H → L (100%)
	357	0.1438	H → L+3 (95.70%)
	358	0.1360	H → L+1 (95.93%)
DTP-OFTPASMe2	361	0.0449	H → L+1 (93.19%)
	367	0.1007	H−2 → L (95.15%)
	457	2.3619	H → L (97.88%)



Figure S3. Single-crystal molecular structure of DTP-OFTPASMe2 (CCDC No. 2302335).

Compound	DTP-OFTPASMe2
Formula	C58H49.33F2N3OS6
CCDC NO	2302335
Formula. wt.	1034.70
Crystal system	triclinic
Space group	<i>P</i> -1
a (Å)	15.01822(14)
<b>b</b> (Å)	15.09567(13)
<i>c</i> (Å)	35.0220(3)
α (°)	93.6909(7)
β (°)	101.5017(8)
γ (°)	99.7237(8)
V(A <sup>3</sup> )	7629.01(12)
Ζ	6
Density/Mgm <sup>-3</sup>	1.351
Abs. Coeff/mm <sup>-1</sup>	2.901
Total no. of reflections	32027
Reflections, $I > 2\sigma(I)$	28729
Max. 2θ (°)	79.376
Complete to 20 (%)	0.78
Data/ Restraints/Parameters	140/2024
Goof (F2)	1.052
R indices $[I \ge 2\sigma(I)]$	0.0316
R indices (all data)	0.0515

 Table S2. Crystallographic parameters for DTP-OFTPASMe2 at 296(2) K



Figure S4. (a–d) Plots of  $J_{sc}$ ,  $V_{oc}$ , FF, and PCE of PSCs as a function of the weight concentration (mg/mL) of DTP-OFTPASMe2 solutions used for spin-coating.

Table S3.	Photovoltaic average parameters of undoped PSCs.

Hole transport material	$J_{ m SC}$	V <sub>OC</sub>	FF	PCE
	(mA cm <sup>-2</sup> )	(V)		(%)
CPDT-OFTPASMe2	$17.9\pm0.9$	$0.97\pm0.01$	$0.26\pm0.01$	$4.6\pm0.4$
TTT-OFTPASMe2	$22.5\pm0.5$	$1.10\pm0.05$	$0.22\pm0.02$	$5.5\pm0.8$
ThoEt-OFTPASMe2	$21.2\pm0.7$	$1.01\pm0.03$	$0.35\pm0.04$	$7.7\pm0.9$
DTP-OFTPASMe2	$19.1\pm3.7$	$0.99\pm0.09$	$0.24\pm0.04$	$4.7\pm1.7$
Spiro-OMeTAD	$18.0\pm0.1$	$0.97\pm0.01$	$0.27\pm0.01$	$4.7\pm0.1$



**Figure S5.** (a–c) Evolution of photovoltaic parameters of unsealed DTP-OFTPASMe2based PSCs, illustrating shelf stability in air at room temperature.



Figure S6. Shelf stability of unsealed PSCs with chemically doped and undoped HTM layers.



**Figure S7.** (a-d) Shelf stability of unsealed PSCs with the undoped DTP-OFTPASMe2 HTM layer in the air.



Figure S8. <sup>1</sup>H NMR spectrum of compound 3 in deuterated chloroform.



Figure S9. <sup>13</sup>C NMR spectrum of compound 3 in deuterated chloroform.



Figure S10. <sup>1</sup>H NMR spectrum of compound 4 in deuterated chloroform.



Figure S11. <sup>13</sup>C NMR spectrum of compound 4 in deuterated chloroform.



Figure S12. <sup>1</sup>H NMR spectrum of compound 5 in deuterated chloroform.



Figure S13. <sup>13</sup>C NMR spectrum of compound 5 in deuterated chloroform.



Figure S14. <sup>1</sup>H NMR spectrum of compound 7 in deuterated chloroform.



Figure S15. <sup>13</sup>C NMR spectrum of compound 7 in deuterated chloroform.



Figure S16. <sup>1</sup>H NMR spectrum of CPDT-OFTPASMe2 (8) in deuterated chloroform.



Figure S17. <sup>13</sup>C NMR spectrum of CPDT-OFTPASMe2 (8) in deuterated chloroform.



Figure S18. Mass spectrum of CPDT-OFTPASMe2 (8).



Figure S19. <sup>1</sup>H NMR spectrum of TTT-OFTPASMe2 (12) in deuterated chloroform.



Figure S20. <sup>13</sup>C NMR spectrum of TTT-OFTPASMe2 (12) in deuterated chloroform.



Figure S21. Mass spectrum of TTT-OFTPASMe2 (12).



Figure S22. <sup>1</sup>H NMR spectrum of ThOEt-OFTPASMe2 (13) in deuterated chloroform.



Figure S23. <sup>13</sup>C NMR spectrum of ThOEt-OFTPASMe2 (13) in deuterated chloroform.



Figure S24. Mass spectrum of ThOEt-OFTPASMe2 (13).



Figure S25. <sup>1</sup>H NMR spectrum of DTP-OFTPASMe2 (14) in deuterated chloroform.



Figure S26. <sup>13</sup>C NMR spectrum of DTP-OFTPASMe2 (14) in deuterated chloroform.



## **Table S4.** Cost evaluation for DTP-OFTPASMe2 synthesis.

	Amount	Amount	Price JPY	Total	Target
Reagent	(g)	(mL)	(g or mL)	Cost	product
				(JPY)	(JPY/g)
3-Fluoroaniline	5		5g - 3960 JPY	3960	
4-Bromothioanisole	22.70		25g-4680 JPY	4249	
t-BuOK	26		100g - 4100	1066	
			JPY		
P(t-Bu) <sub>3</sub>	0.362		5g-32,900 JPY	2381	
Pd <sub>2</sub> (dba) <sub>3</sub>	0.41		5g-33,210 JPY	2723	
Toluene		80	500  mL - 950	152	
			JPY		
CHCl <sub>3</sub>		1800	25 kg -17,700	1274	
			JPY		
Silica gel	500		25 kg -114,000	2280	
			JPY		
Hexane		600	15 kg - 6,350	254	
			JPY		
Total				17339	Produt-3
					(867
					JPY/g)
3-Fluoro-N,N-bis(4-	20		1g – 867JPY	17340	
(methylthio)phenyl)aniline (3)					
NBS	11		100 g 3030	333	
			JPY	555	
DMF		50	500 mL - 1760 JPY	176	
CHCl <sub>3</sub>		1800	25 kg - 17,700 JPY	1274	
Silica gel	400		25 kg - 114,000	1824	
Hexane		600	15 kg - 6,350 JPY	254	

Total				21,201	Produt-4
					(848JPY/g)
			Price JPY	Total	Target
Reagent	Amount (g)	Amount (mI)	(g or mL)	Cost	product
	(g)			(JPY)	(JPY/g)
4-Bromo-3-fluoro-N,N-bis(4-			1g – 848 JPY	10,176	
(methylthio)phenyl)aniline (3)					
	12				
Bis(pinacolato)diboron	7		25g – 7500 JPY	2,100	
CH <sub>3</sub> COOK	13.5		500g – 2430	66	
			JPY		
Pd(dppf)Cl <sub>2</sub>	3		5g – 28100 JPY	16,860	
Dioxane		80	500 – 1760 JPY	281	
CHCl <sub>3</sub>		1800	25kg -17,700	1274	
			JPY		
Hexane		600	15 kg – 6,350	254	
			JPY		
Silica gel	500		25 kg -114,000	2280	
			JPY		
Total				33,291	Produt-5
					(4755
					JPY/g)



Table S5.	Cost	evaluation	for	DTP-	OFTPA	SMe2	synthesis.
							-

	Amount	Amount	Price JPY	Total	Target
Reagent	(g)	(mI)	(g or mL)	Cost	product
	(g)	(IIIL)		(JPY)	(JPY/g)
2,6-Dibromo-4-(4-	0.2		1g – 2343	468	
methoxyphenyl)-4H-			JPY		
dithieno[3,2-b:2',3'-					
d]pyrrole (11)					
3-Fluoro-N,N-bis(4-	0.5		1g – 4755	2378	
(methylthio)phenyl)-4-			JPY		
(4,4,5,5-tetramethyl-1,3,2-					
dioxaborolan-2-yl)aniline					
(5)					
Pd(PPh <sub>3</sub> ) <sub>4</sub>	0.03		5g - 16,300	97.8	
			JPY		
THF		25	500 mL -	102.5	
			2050 JPY		
CHCl <sub>3</sub>		1800	25 kg –	1274	
			17,700 JPY		
Silica gel	300		25 kg –	1368	
			114,000 JPY		
Total				5688	Produt-14
					(16,251
					JPY/g)

However, to account for several important parameters (e.g., energy consumption, waste treatment, and labor), a multiplication factor of 1.5 was applied, resulting in a more realistic estimation of the lab synthesis cost of approximately 24,376 JPY/g. This is about one-third the cost of purified spiro-OMeTAD (~66,500 JPY/g, high purity, Ossila).

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