新規シアノ置換スピロ型ドーパントフリーホール輸送材料を用いたペロブスカイト太陽電池

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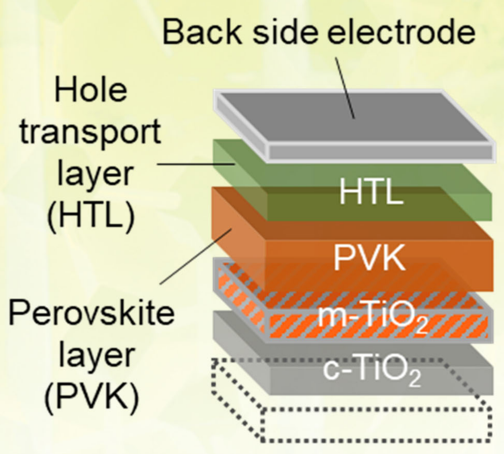
Introduction

Perovskite solar Cell (PSC)

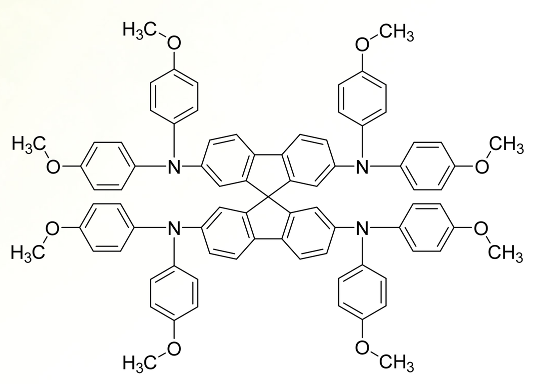


・High power conversion efficiency
・Easy fabrication
・Low cost

HTMs have been actively explored. The exploration mainly focused on the following three characteristics:
1) Long-term stability.
2) High hole mobility.
3) Suitable frontier energy levels matching that of perovskite layer.

Figure. 1 Typical mesoporous-type device structure.

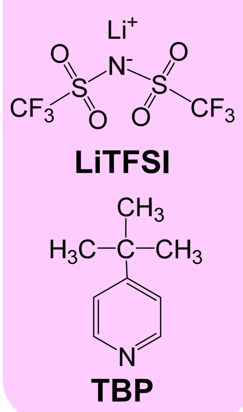
Typical organic HTM for PSC



Spiro-OMeTAD

Some dopants (ionic compound, base etc.,) are needed to introduce more charge carriers.

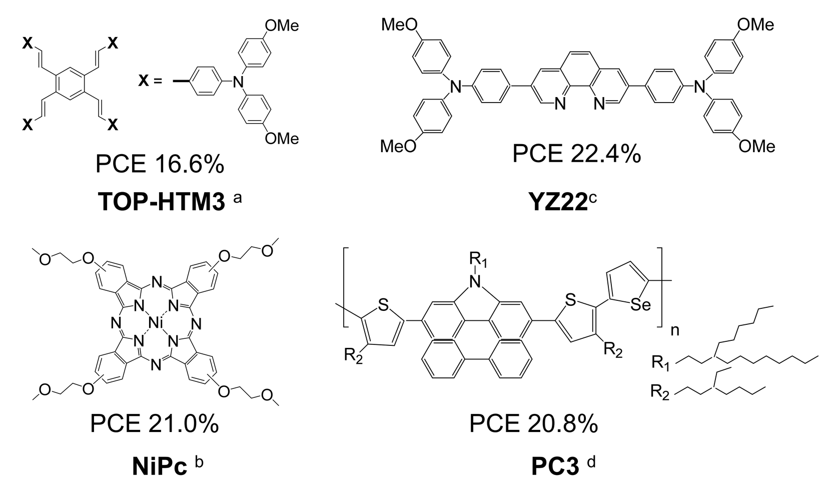
Dopants



Hygroscopic, volatile
Device degradation

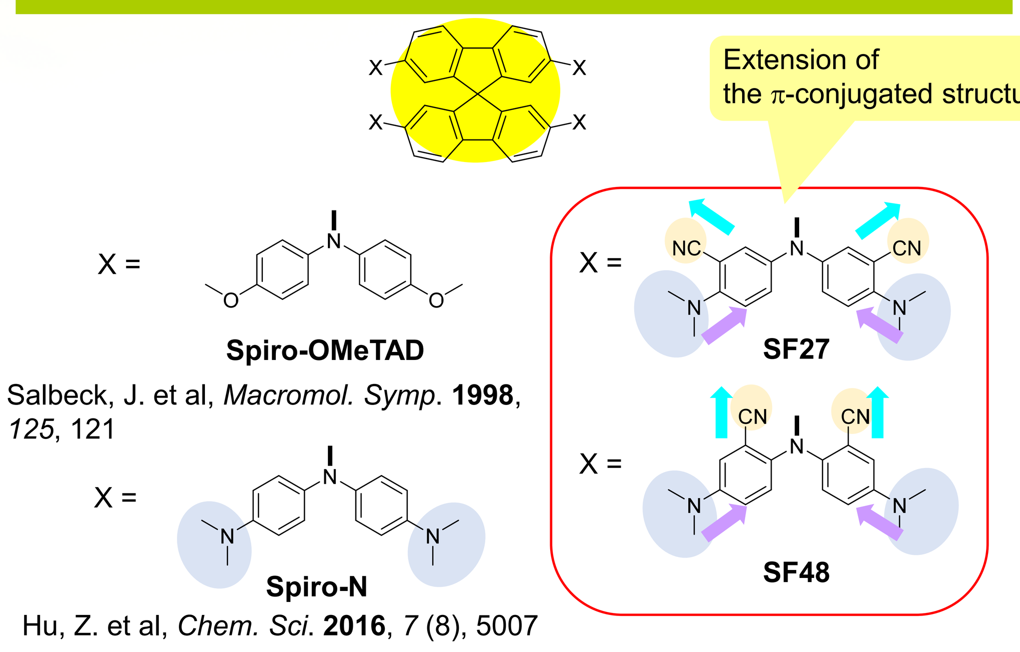
Previous Work

Dopant-free HTMs



[a] Hidetaka Nishiura, et al., *ACS Appl. Mater. Interfaces* **2020**, 12, 32994.
[b] Zefeng Yu, et al., *Angew. Chem. Int. Ed.* **2021**, 60, 6294.
[c] By Xiaomin Zhao, et al., *Energy. Environ. Sci.* **2020**, 13, 4334.
[d] Zhaoyang Yao, et al., *J. Am. Chem. Soc.* **2020**, 142, 17681.

This Work



Salbeck, J. et al, *Macromol. Symp.* **1998**, *125*, 121
Hu, Z. et al, *Chem. Sci.* **2016**, 7 (8), 5007

Figure 2. Chemical structures of **Spiro-OMeTAD**, reference compound **Spiro-N**, **SF27** and **SF48**.

Chemical Properties

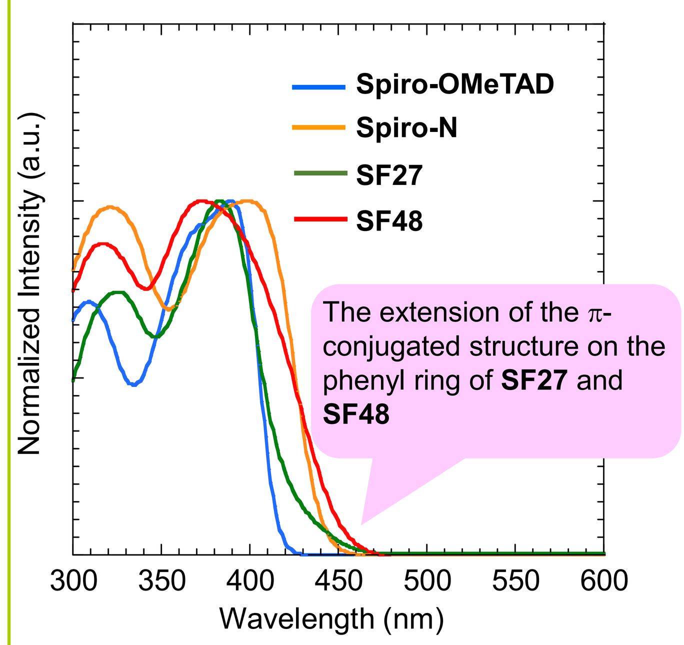
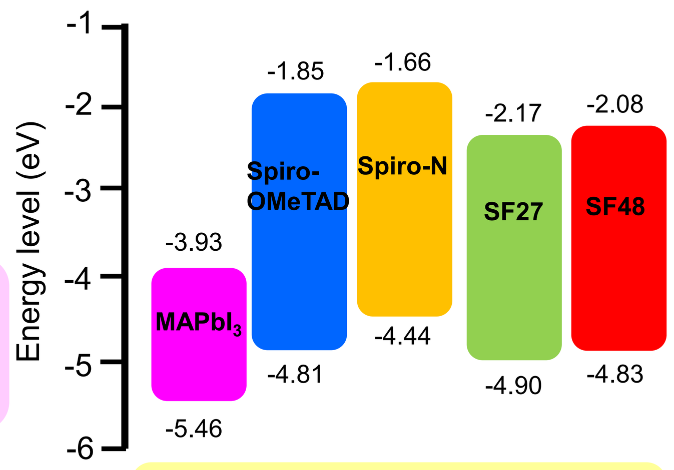


Figure 3. UV-vis spectra of the HTMs in solution (1x10^{-5} M in CB).



SF27 and **SF48** have a suitable HOMO energy levels for hole extraction from perovskite.

Figure 4. Energy diagram of the HTMs.

Table 1. Hole mobility[a] of the HTMs.

	μ_h (cm^{2}V^{-1}s^{-1})
Spiro-OMeTAD	11.9x10^{-5}
Spiro-N	21.4x10^{-5}
SF27	0.5x10^{-5}
SF48	1.7x10^{-5}

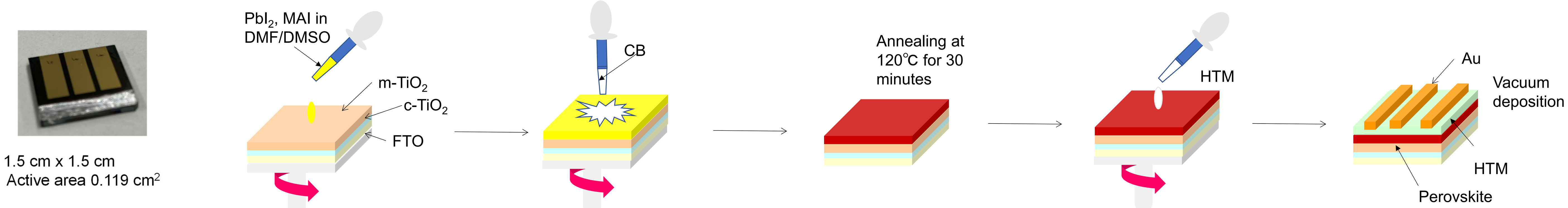
SF27<SF48

[a]The hole mobilities of spin-coated films of the HTMs were estimated via SCLC measurements on an ITO/PEDOT:PSS/HTMs/Au devices.

The hole mobility of **SF48** was higher than that of **SF27**, although it was lower than that of **Spiro-OMeTAD**.

It is necessary to deposit a thin HTL on the perovskite film.

Device Fabrication



1.5 cm x 1.5 cm
Active area 0.119 cm^2

Results and Discussion

1. The photovoltaic data of the PSCs based on non-doped HTMs

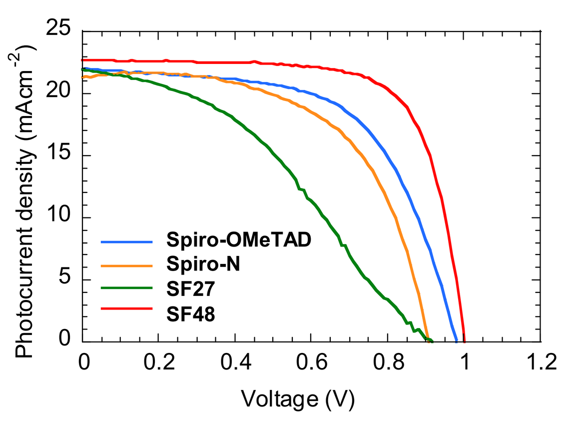


Figure 5. *J-V* curves for the PSCs based on non-doped HTMs as measured under AM 1.5G solar irradiance (100 mW/cm^2) by a backward scan.

Table 2. Photovoltaic parameters of the PSCs for **HTMs** without dopants. (Thickness of HTMs; 50 nm)

	J_{sc} / mA cm^{-2}	V_{oc} / V	FF	PCE / %
Spiro-OMeTAD	22.0	0.98	0.60	12.9
Spiro-N	20.0	0.92	0.66	12.1
SF27	21.9	0.92	0.38	7.6
SF48	22.7	1.00	0.72	16.3

The PSC based on non-doped **SF48** exhibited the best PCE.

SF48>Spiro-OMeTAD,Spiro-N>SF27

2. Dependence on the film thickness of SF48

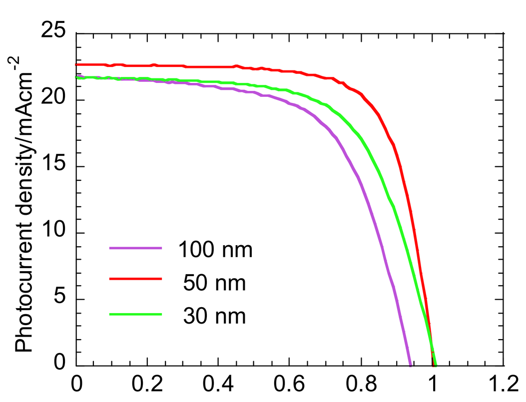


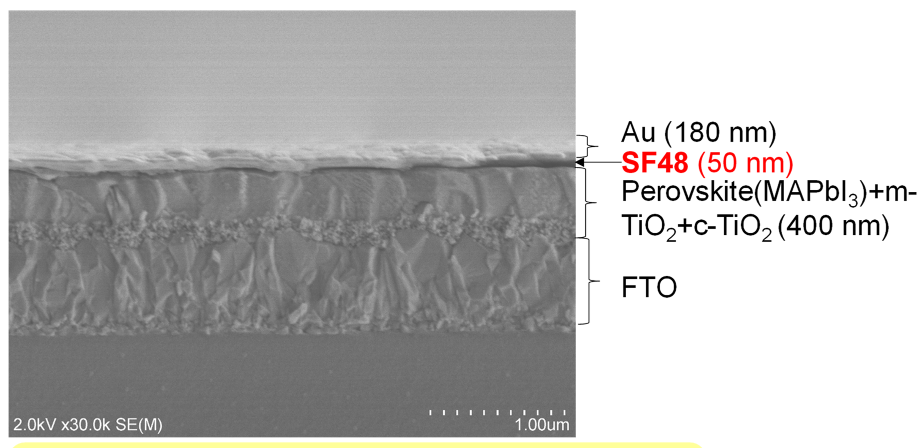
Figure 6. *J-V* curves for the PSCs based on non-doped **SF48** with various thicknesses of **SF48** as measured by a backward scan.

Table 3. Photovoltaic parameters of the PSCs based on non-doped **SF48** with various thicknesses of the HTM.

膜厚/nm	J_{sc} / mA cm^{-2}	V_{oc} / V	FF	PCE / %
100	21.7	0.94	0.62	12.6
50	22.7	1.00	0.72	16.3
30	21.7	1.01	0.64	14.0

The PSCs with a 50 nm HTL layer showed the best PCE.

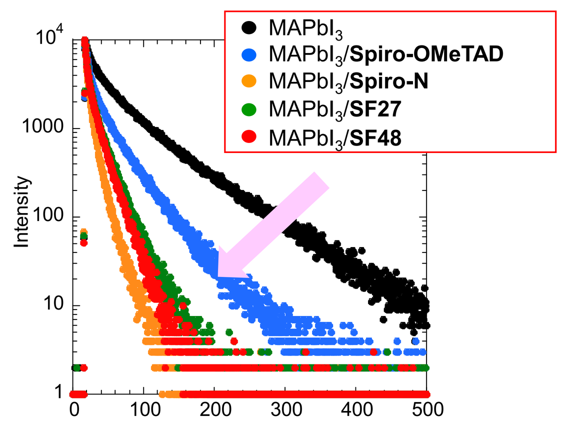
3. SEM image



The optimal thickness of **SF48** was only around 20%.
SF48 is cost effective HTM.

Figure 7. Cross-sectional SEM image of **SF48**-based device.

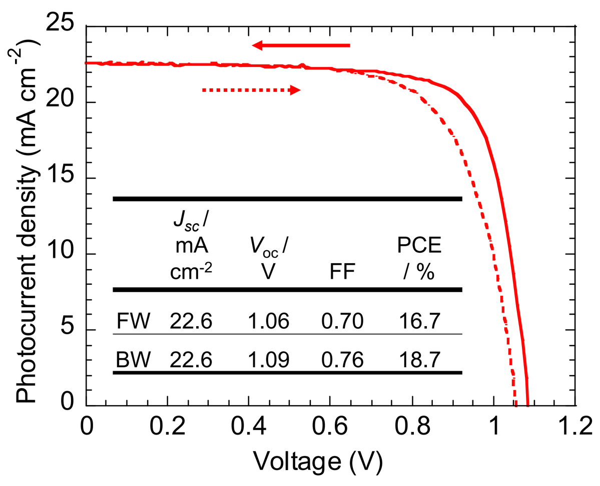
4. Hole extraction ability



SF27, SF48,Spiro-N>Spiro-OMeTAD

Figure 8. TRPL decay curves of the pristine perovskite and perovskite covered with non-doped HTM films excited at 532 nm.

5. The cell performance of the best PSC



	J_{sc} / mA cm^{-2}	V_{oc} / V	FF	PCE / %
FW	22.6	1.06	0.70	16.7
BW	22.6	1.09	0.76	18.7

Figure 9. *J-V* curve for the highest efficiency solar cell based on non-doped **SF48**.

Table 4. Photovoltaic parameters of the PSCs with $Cs_{0.05}(FA_{0.85}MA_{0.15})_{0.95}Pb(I_{0.89}Br_{0.11})_3$ as the perovskite layer[a].

	J_{sc} / mA cm^{-2}	V_{oc} / V	FF	PCE / %
Spiro-OMeTAD with dopant (TBP, LiTFSI)				
FW	22.2±0.4	1.13±0.01	0.68±0.04	17.1±1.1
BW	20.7±1.3	1.10±0.03	0.71±0.03	16.1±1.5
SF48 without dopant				
FW	22.5±0.4	1.05±0.02	0.65±0.03	15.3±0.9
BW	22.4±0.4	1.08±0.01	0.73±0.02	17.6±0.6

[a] Passivated with octylammonium iodide between the perovskite and HTL.

The PCE is higher than that for the doped **spiro-OMeTAD**-based PCEs.

6. Thermal stability test

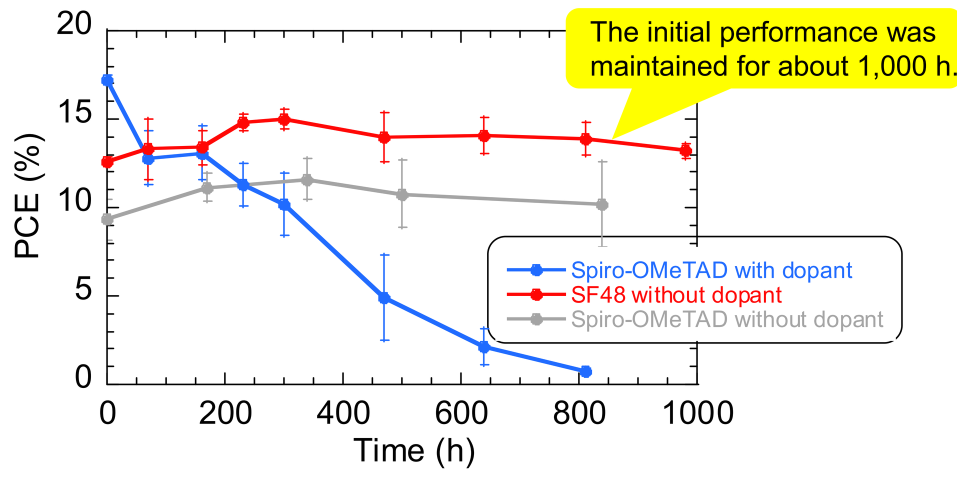


Figure 10. Change in the efficiencies of the solar cells based on doped (blue) and non-doped **Spiro-OMeTAD** (grey), and non-doped **SF48** (red) at 85 ℃ in ambient air. The PCEs were provided by backward scans.

Summary

We have successfully synthesized and characterized cyano-substituted spiro-typed compounds, **SF27** and **SF48**, for use as HTMs in PSCs. PSCs with non-doped **SF48** exhibited a high PCE of 18.7%, which was comparable to the reference PSC with doped **Spiro-OMeTAD** (18.6%). In addition, the thermal stability of **SF48** at 85° C in ambient air was superior to **Spiro-OMeTAD**, both with and without dopants.[1] Therefore, the **SF48** spirobifluorene-based compound is determined to be quite effective as a high-performance dopant-free HTM for PSCs.

[1] N. Onozawa-Komatsuzaki, D. Tsuchiya, S. Inoue, A. Kogo, T. Funaki, M. Chikamatsu, T. Ueno and T. N. Murakami, ACS Appl. Energy Mater. **5**, 6633 (2022).