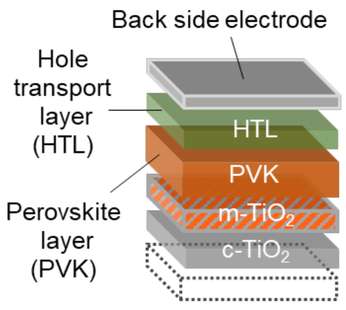
非ハロゲン系溶媒に可溶なドーパントフリーホール輸送材料を用いたペロブスカイト太陽電池

Introduction

Perovskite solar Cell (PSC)



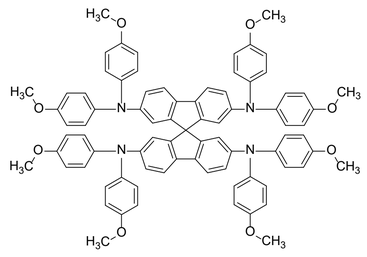
- High power conversion efficiency
- Easy fabrication
- Low cost

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.

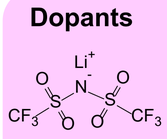
Typical organic HTM for PSC

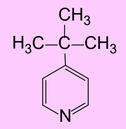


Spiro-OMeTAD

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

Dopants





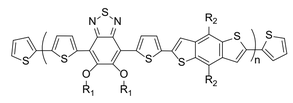
Hygroscopic, volatile

Device degradation

Most of organic HTMs are processed with chlorinated solvents such as chlorobenzene(CB).

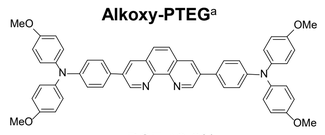
Nonhalogenated-solvent (green-solvent)-soluble, dopant-free HTMs are desirable for the practical application of PSCs.

Green-solvent-soluble dopant-free HTMs



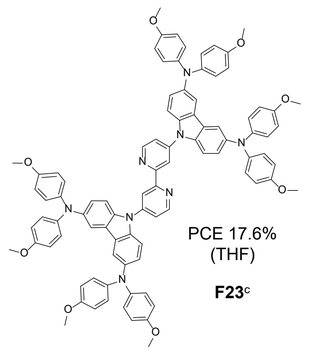
PCE 19.9%
(3-methylcyclohexanone)

Alkoxy-PTEG[a]



PCE 19.2%
(Ethyl acetate, Inverted cell)

M1[b]

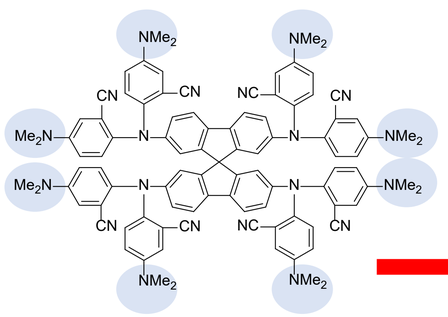


PCE 17.6%
(THF)

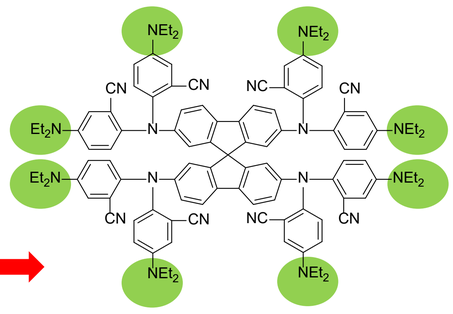
F23[c]

[a] J. Lee et al, *Adv. Energy Mater.,* **2020**, 10, 1902662.
[b] J. Huang et al, *J. Mater. Chem. C.,* **2021**, 9, 8930.
[c] H.Lu et al, *Energy. Environ. Sci.,* **2020**, 385, 123976.

Our Work



SF48[a]



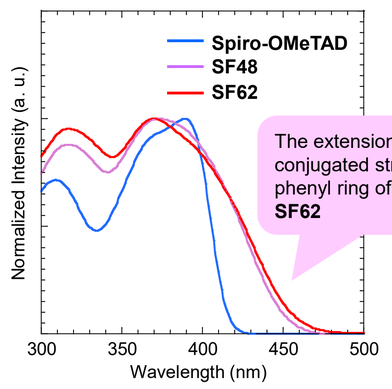
SF62

orting

ITM.)

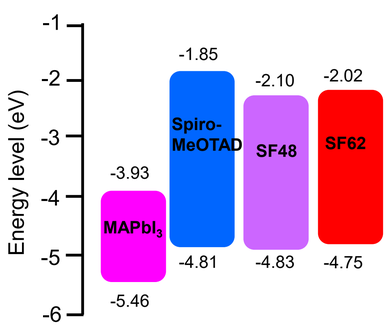
SF62 is soluble in green solvent such as AcOEt because of large hydrophobic groups.

[a] Nobuko Onozawa-Komatsuzaki et al, *ACS Appl. Energy Mater.* **2022**, 5, 6633



The extension of the π-conjugated structure on the phenyl ring of **SF48** and **SF62**

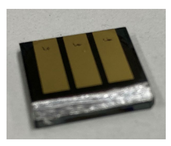
Figure 2. UV-vis spectra of the HTMs in solution (1x10^{-5} M in CB).



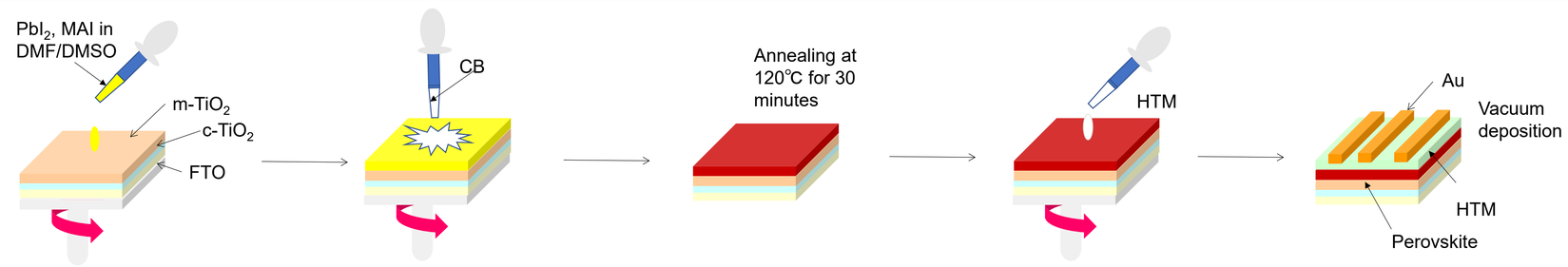
SF48 and **SF62** have a suitable HOMO energy levels for hole extraction from perovskite.

Figure 3. Energy diagram of the HTMs.

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

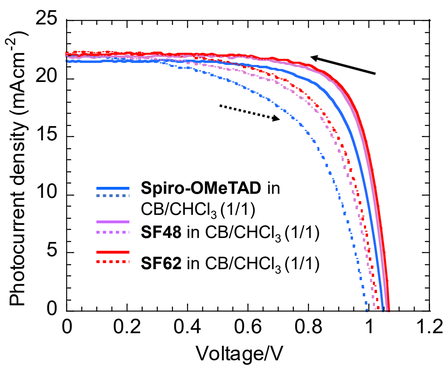


Figure 4. *J–V* curves for the PSCs with non-doped **Spiro-OMeTAD**, **SF48**, and **SF62** using CB/$CHCl_3$ (1/1) as the solvent.

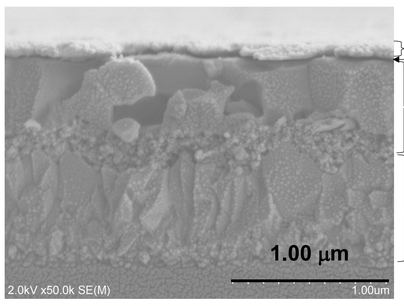
Table 1. Photovoltaic parameters of the PSCs for **HTMs** without dopants. (Thickness of HTMs; 20 nm)

	J_{sc} / mA cm^{-2}	V_{oc} / V	FF	PCE / %
Spiro-OMeTAD	21.9	0.99	0.57	12.5
SF48	22.4	1.01	0.67	15.2
SF62	21.8	1.03	0.67	15.1

The PSC based on non-doped **SF48, 62** exhibited the higher PCE than that of **Spiro-OMeTAD**.

SF48, SF62>Spiro-OMeTAD

2. SEM image

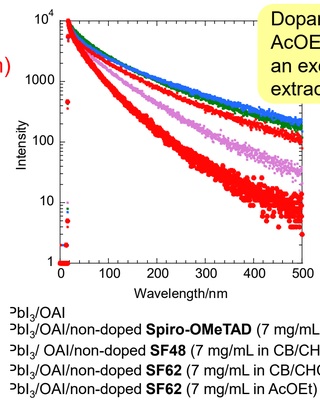


Au (180 nm)
n-octylammonium iodide (OAI)+**SF62** (20 nm)
Perovskite ($MAPbI_3$)+ mp-TiO_2+c-TiO_2 (650 nm)
FTO

The optimal thickness of **SF62** was only around 10%. **SF62** is cost effective HTM.

Figure 5. Cross-sectional SEM image of **SF62**-based device.

3. Hole extraction ability



Dopant-free **SF62** using AcOEt as the solvent has an excellent hole extraction capability.

Figure 6. TRPL decay curves of the pristine perovskite and perovskite covered with non-doped HTM films excited at 532 nm.

4. The cell performance of the best PSC

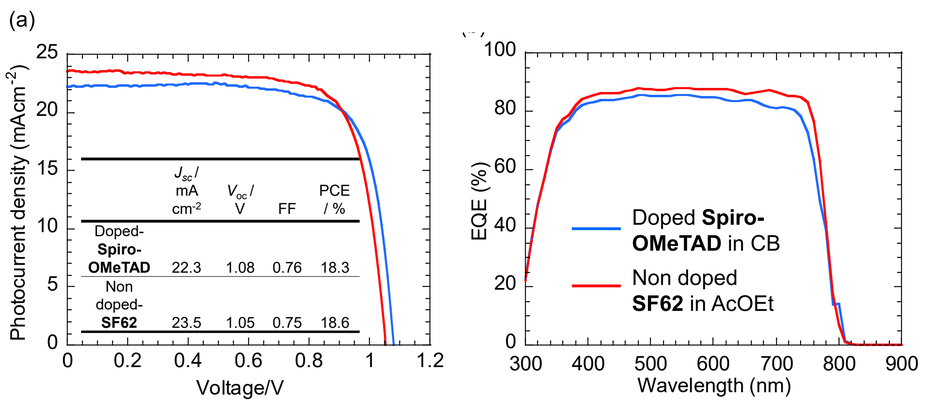


Figure 7.(a) *J–V* curves for the best-performing PSCs with non-doped **SF62** using AcOEt as the solvent, along with doped **Spiro-OMeTAD** using CB as a reference and (b) EQE spectra of the same PSCs.

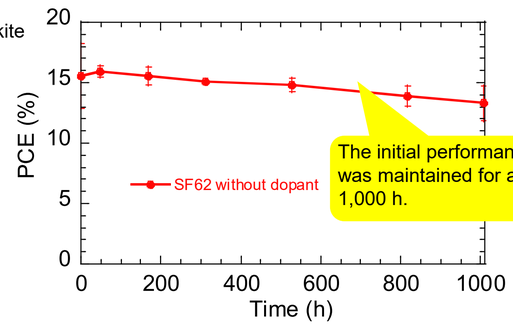
Table 2. Photovoltaic parameters of the PSCs with $MAPbI_3$ as the perovskite layer[a].

	J_{sc} / mA cm^{-2}	V_{oc} / V	FF	PCE / %
Spiro-OMeTAD with dopant (TBP, LiTFSI)				
FW	22.5 ± 0.5	1.02 ± 0.02	0.61 ± 0.02	14.0 ± 0.6
BW	22.0 ± 0.6	1.07 ± 0.02	0.73 ± 0.03	17.2 ± 0.9
SF62 without dopant				
FW	23.0 ± 0.3	0.99 ± 0.02	0.63 ± 0.04	14.2 ± 1.1
BW	22.9 ± 0.3	1.04 ± 0.01	0.74 ± 0.02	17.7 ± 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.

5. Thermal stability test



The initial performance was maintained for about 1,000 h.

Figure 8. Change in the efficiencies of the solar cells based on non-doped **SF62** at 85 ℃ in ambient air.

Summary

We developed a new compound **SF62** and successfully applied it as a dopant-free HTM in PSCs. In particular, the HTL layer of **SF62** was prepared using the nonhalogenated green solvent AcOEt. Consequently, the PCE of the device based on **SF62** was 18.6%, comparable to that of the reference PSC with doped **Spiro-OMeTAD** (18.3%). Furthermore, the thermal stability of the PSC based on non-doped **SF62** at 85 °C in ambient air was found to be superior to that of doped or non-doped **Spiro-OMeTAD**. [1]

[1] N. Onozawa-Komatsuzaki, D. Tsuchiya, S. Inoue, A. Kogo, T. Ueno and T. N. Murakami, *Appl. Phys. Express,* **2023**, 16, 016502.

小野澤伸子1、土屋大輔2、井上真一2、古郷敦史1、村上拓郎1
1.産業技術総合研究所 ゼロエミッション国際共同研究センター，2.日本精化株式会社

AIST 太陽光発電研究成果報告 2023

産総研

NIPPON FINE CHEMICAL CO.,LTD.