Efficient and stable planar perovskite solar cells with a non-hygroscopic small molecule oxidant doped hole transport layer

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Abstract: We report planar heterojunction perovskite solar cells with tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) doped spiro-MeOTAD by solvent treatment as hole transport layer. The non-hygroscopic F4-TCNQ doped spiro-MeOTAD plays the same role as Li-bis (trifluoromethanesulfonyl) imide doped spiro-MeOTAD in perovskite solar cells, endowing the device both high efficiency and good stability. The F4-TCNQ dopant was optimized to enhance the conductivity and adjust the highest occupied molecular orbital of spiro-MeOTAD to match the valence band maximum of perovskite for efficient hole extraction, which results in a high fill factor, open circuit voltage and short current density, simultaneously. Device including the F4-TCNQ doped spiro-MeOTAD exhibits a power conversion efficiency of 10.59%, which is a 160% improvement relative to that of the control device with the pristine spiro-MeOTAD as hole transport layer. Time-dependent solar cell performance measurements revealed significantly improved air stability for perovskite solar cells with the F4-TCNQ doped spiro-MeOTAD hole transport layer.

Keywords: Perovskite solar cells, F4-TCNQ doped spiro-MeOTAD, Ground state charge transfer, High performance, Stability

1. Introduction

Organometal halide perovskites ABX_3 ($A = CH_3NH_3$, $B = Pb$, and $X = Br, Cl, \text{ or } I$) based solar

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1 cells (PVKSCs) have emerged as a dark horse in the photovoltaic field due to their simple low
2 cost fabrication process and unprecedented rapid growth of efficiency [1-3]. Among various
3 configurations, planar heterojunction perovskite solar cells (PH PVKSCs) with their simple
4 structure and preparation process have received the most attention. Through elaborate interface
5 engineering the recent breakthrough of PH PVKSCs gave a power conversion efficiency (PCE) of
6 19.3% [4]. Presently there are many reports about optimizing functional layers, such as electron
7 transport layer (ETL) [5] and hole transport layer (HTL) [6,7], to improve device performance.
8 For the use of HTL, there are two concerns. On the one hand, the HTL-free PVKSCs were
9 proposed in view of the high price of the widely used 2,2',7,7'-tetrakis
10 (N,N-di-*p*-methoxyphenylamine)-9,9-spirobifluorene (spiro-MeOTAD) hole transport material
11 and the viewpoint that perovskite intrinsically inclined to behave as p-type semiconductor [8-10].
12 Recently, Liu's and Ke's works both demonstrated the ETL-free PH PVKSCs with high
13 efficiencies of 13.5% and 14.14%, respectively [11,12]. Anyway, their performance of these
14 HTL-free or ETL-free PVKSCs are not so good as their comparators which have the functional
15 layers [4]. On the other hand, spiro-MeOTAD is still a suitable candidate for PVKSC applications
16 [13] because of its several desirable properties including glass transition temperature ($T_g=120\text{ }^{\circ}\text{C}$),
17 solubility, ionization potential, absorption spectrum, and solid-state morphology. However, similar
18 with other organic hole transporters, spiro-MeOTAD presents low conductivity in its pristine form.
19 To overcome this problem additional charge carriers should be generated to enhance the
20 conductivity by ionic doping technique. PVKSCs base on Li-bis (trifluoromethanesulfonyl) imide
21 (Li-TFSI) doped spiro-MeOTAD (LS) HTL presented excellent performance, but the extremely
22 hygroscopic nature of lithium salt seriously accelerates the decomposition of perovskite and
23 degradation of the device performance. The presence of pinhole channels originating from the
24 migration of Li-TFSI from the bottom to the top across the spiro-MeOTAD film can seriously
25 promote the degradation processes of solar cells [14]. The embarrassed situation we are
26 encountering is that LS HTL makes sure the high device efficiency, while the inevitable
27 introduction of acetonitrile (ACN) and 4-tert-butylpyridine (TBP) with Li-TFSI seriously destroys
28 perovskite films and thus device stability (**Fig. 1S and Fig. 2S**). Synthesizing new HTL materials
29 to replace spiro-MeOTAD is growing and encouraged efficiencies are achieved, but whether the
30 synthesis method is simple or not and whether it is suitable for large-scale use is not mentioned

[15].

Nevertheless, the p-i-n device architecture with both HTL and ETL simultaneously is still the best choice when repeatable high efficiency with excellent stability is needed [16-19]. Based on the above considerations, to further promote the industrialization of PH PVKSCs, it still needs to further simplify the device processing procedures as well as to improve the device stability but not in the cost of excess sacrificing of device efficiency. In previous research experience, solution-based chemical doping is an important strategy to alter the charge-transport properties of both molecular and polymeric organic semiconductors, which was widely applied in organic electronic field [14,20,21]. This is achieved by the charge transfer processes that could dramatically enhance the conductivity through intentional solution-based chemical doping. Here, by intentional solution chemical doping, we demonstrated high efficient PH PVKSCs with enhanced stability. The p-type doping by tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) actually enhanced the conductivity of spiro-OMeTAD and induced the favorable shift of Fermi level and HOMO level of spiro-OMeTAD, resulting in more favorable charge transport in bulk spiro-OMeTAD film and charge separation at the perovskite/spiro-OMeTAD interface, thus an open circuit voltage (V_{OC}) of 0.946 V, a short current density (J_{SC}) of 18.72 mA/cm² and a fill factor (FF) of 56.82% combined with a PCE of 10.59% were demonstrated. Furthermore, the non-hygroscopic F4-TCNQ doped HTL endows the device better stability.

2. Experiments

2.1. Materials

Lead chloride (PbCl₂, 99.999%, obtained from Sigma-Aldrich) and CH₃NH₃I (provided by Shanghai Materwin New Materials Co. Ltd) mixed with molar ratio of 1:3 were dissolved in N, N-Dimethylformamide (DMF) with a concentration of 38%. The precursor solution was stirred at 60 °C overnight before use. The hole transport layer (HTL) solution was prepared by dissolving 72.3 mg spiro-MeOTAD (99.8%, bought from Shenzhen Feiming Science and Technology Co., Ltd) in 1 ml chlorobenzene (CB) and then mixed with F4-TCNQ/CB solution with a concentration of 1 mg/mL (or 1 μg/μL). For comparison, 1 mL of 72.3 mg/mL pristine spiro-MeOTAD/CB solution and 1 mL of 72.3 mg/mL spiro-MeOTAD/CB solution mixed with 28.8 μL 4-tert-butylpyridine (TBP, purchased from Sigma-Aldrich) and 17.5 μL of a stock solution of 520

mg/mL Li-bis (trifluoromethanesulfonyl) imide (Li-TFSI, purchased from Acros) in acetonitrile (ACN) were also prepared. The TiO₂ nanocrystals were synthesized from a sol-gel method described elsewhere [22 (a)].

2.2. Solar cell device fabrication

All the device fabrication was processed in glove box filled with N₂ except for the compact TiO₂ (c-TiO₂) covered substrate. The patterned FTO substrates (Nippon, 14 Ω/□) were cleaned with deionized water, ethanol and acetone and then subjected to an ozone-ultraviolet treatment for 15 min. A 40 nm thick c-TiO₂ layer was spin-coated on the substrates using the sol-gel solution synthesized above with a spin speed and time of 4000 rpm/25 s. The c-TiO₂ layer was then annealed at 450 °C for 30 min. Before using, the substrates were treated in a aqueous solution of TiCl₄ (0.04 M) at 70 °C for 30 min, then rinsed with deionized water and dried at 120 °C for 15 min. Afterwards, the substrates were transferred into glove box for the deposition of perovskite. To deposit the perovskite layer, the precursor solution was spin-coated on the FTO/c-TiO₂ substrates at 2000 rpm for 40-50 s and then annealing the as-casted film from 20 °C to 95 °C with duration of 90 minutes [22 (b)].

Once perovskite thin films grow well, the HTL solution was spin-coated at 2800 rpm for 30 s. For device of the control group, 1 mL spiro-OMeTAD/CB (72.3 mg/mL) solution was employed with addition of 17.5 μL Li-TFSI/ACN (520 mg/mL), and 28.8 μL TBP. As a comparison, 1 mL F4-TCNQ/CB (1 mg/mL, or 1 μg/μL) was used as dopant solution, for different doping ratio, corresponding amount of volume of the F4-TCNQ/CB solution was adopted. Lastly, to form the back contact, a 120 nm thick silver layer was thermally evaporated on top of the device under a pressure of 5×10^{-6} Torr. The devices fabricated have a layered p-i-n configuration glass/FTO/compact TiO₂ (c-TiO₂)/CH₃NH₃PbI_{3-x}Cl_x (PVK)/spiro-MeOTAD/Ag, which consists of ~450 nm thick FTO electrode, ~40 nm of TiO₂, ~400 nm of perovskite, ~400 nm of spiro-MeOTAD, and ~120 nm of Ag.

2.3. Characterizations and measurements

A VARIAN Cary 5000 UV-Vis-NIR spectrophotometer was used to record the UV-Vis absorption spectra of the perovskite films. A Bruker AXS D8 Advance X-ray diffractometer was used to obtain the X-ray diffraction (XRD) pattern (2θ scans) of the perovskite films deposited on the glass/FTO/c-TiO₂ substrates using Cu-Kα radiation (λ = 1.54050 Å). A Hitachi SU-70

scanning electron microscope (SEM) was adopted to confirm the top view images and thicknesses of the deposited perovskite films.

Linear current density-voltage (J - V) curves of the FTO/PEDOT:PSS/HTL/Ag hole only devices were obtained for the conductivity measurements by testing in ambient conditions with a sourcemeter (Keithley 2400, USA) in a two-point contact setup. The J - V measurements of PVKSCs were conducted under simulated AM 1.5G sunlight of 100 mW/cm^2 using an AM 1.5G type filter (Newport, 81904, USA). The light intensity was adjusted by using a standard Si cell. J - V curves were obtained by applying an external bias to the cell, and measurements were recorded with a Keithley model 2400 digital source meter at room temperature in the ambient air. The effective area of the cell was defined to be 0.07 cm^2 by a non-reflective metal mask.

3. Results and discussion

(Fig. 1)

Fig.1 shows the UV-Vis absorption spectra of pristine spiro-MeOTAD, the mixture of spiro-MeOTAD and F4-TCNQ with gradual molar ratio (Generally, a molar ratio of spiro-MeOTAD: F4-TCNQ = 100:1 corresponds to a weight ratio of 100:0.23) and the mixture of spiro-MeOTAD and Li-TFSI (weight ratio spiro-MeOTAD:Li-TFSI=100:13, corresponding to a molar ratio of 100:55) in chlorobenzene (CB). The inset of Fig.1 gives the photograph of the solutions spiro-MeOTAD/CB (S), spiro-MeOTAD:Li-TFSI/CB (LS), F4-TCNQ/CB (F) and spiro-MeOTAD:F4-TCNQ/CB (FS) dressed in a cuvette. The good solubility of spiro-MeOTAD and F4-TCNQ in chlorobenzene, as shown by the uniform reddish brown spiro-MeOTAD:F4-TCNQ/CB solution, ensures that F4-TCNQ will mix well with Spiro-MeOTAD in the solid state Spiro-MeOTAD film and uniform bulk doping will take place. The absorption peak maximum of spiro-MeOTAD and F4-TCNQ is at $\sim 380 \text{ nm}$ and $\sim 390 \text{ nm}$ (**Fig. 3S**), respectively, which are ascribed to the light absorption induced π - π^* transition. Upon mixing spiro-MeOTAD and F4-TCNQ, as shown in **Fig. 1**, two distinctive new absorption bands appear with peak maxima located at $\sim 525 \text{ nm}$ and $\sim 765 \text{ nm}$, indicating the occurrence of ground state charge-transfer from the HOMO level of spiro-OMeTAD to the LUMO level of F4-TCNQ. The absorption peak of $\sim 525 \text{ nm}$ belongs to oxidized spiro-OMeTAD, which is generated in the solution by p-type doping [23-26]. It should be noted here that the absorption peak of the

oxidation state spiro-MeOTAD is independent on the dopant adopted. Generally, an absorption peak always appears as long as the dopant including Co complex (FK102 or FK209) [7], O₂ [14,24], or SnCl₄ [25]) can oxidize spiro-OMeTAD. These have been proved by theoretical calculations [23] and actual experiments [7,14,24,25,26,28]. Compared with the previous works, our results suggest the expensive Co complex can be well substituted by the cheap F4-TCNQ. Generally, the absorption of the oxidized spiro-MeOTAD in the wavelength range of 500-700 nm is similar to the radical cation absorption of a derivative of spiro-MeOTAD and it is because of this green light wavelength range absorption that the color of spiro-OMeTAD solution changes to red-brown. While the F4-TCNQ⁻ reveals a distinct absorption profile ranging from 580 nm to 1000 nm with an absorption peak of ~765 nm. Therefore, at <700 nm it is difficult to differentiate the negative polaron absorption of F4-TCNQ from the absorption bands of the oxidized spiro-MeOTAD. Nevertheless, it is obvious that the absorption spectrum greater than 700 nm is mainly ascribed to the negative F4-TCNQ polaron absorption. Moreover, the height of the oxidized absorption peak of spiro-OMeTAD that corresponds to the concentration of oxidized spiro-OMeTAD improves super-linearly with increasing content of F4-TCNQ below doping ratio of 1%. This observation suggests that F4-TCNQ has strong ability to oxidize spiro-OMeTAD. Therefore, F4-TCNQ is able to accept electrons from spiro-OMeTAD in the solid film, consequently generating additional free holes to enhance the conductivity of spiro-OMeTAD film as an efficient p-type dopant. For spiro-MeOTAD:Li-TFSI/CB solution the color is inconspicuous yellowish with little absorption in the above mentioned typical absorption wavelength range of oxidized spiro-OMeTAD, which suggests that Li-TFSI does not really have an oxidation doping effect on spiro-MeOTAD as some literatures reported [21(b)]. Combined our experimental results with previous works, we believe that Li-TFSI has no significant oxidation effect on spiro-MeOTAD and it merely contributes to conductivity of spiro-MeOTAD by lithium ion assisted conductivity as in the lithium-ion battery. The effective electron transfer from spiro-OMeTAD to F4-TCNQ could be illustrated in following equation:

The height of the oxidized absorption peak of spiro-OMeTAD improves non-linearly with increasing content of F4-TCNQ at the doping ratio greater than 1%, suggesting that the doping efficiency [27] or the dissociation efficiency of F4-TCNQ·spiro-MeOTAD charge transfer

complex is not 100%, probably because the low temperature ($T \approx 300$ K) is not enough to provide sufficient thermal activation energy ($k_B T \approx 4.14 \times 10^{-21}$ J).

Due to the exceptional strong electron accepting ability of F4-TCNQ molecules (LUMO level -5.24 eV), p-doping occurred via ground state electron transfer from the HOMO level of spiro-OMeTAD (-5.22 eV) to the LUMO level of F4-TCNQ, leaving holes on the HOMO level of spiro-OMeTAD (**Fig. 4S**), which is accompanied by the immediate color change of spiro-MeOTAD/CB solution from light yellow to dark red-brown (**Fig. 5S**) [20]. This leads to a higher conductivity of spiro-OMeTAD film. To test this hypothesis, we fabricated FTO/PEDOT:PSS/HTL/Ag hole only devices with different HTLs and conducted their I - V measurement. In total, three HTL samples contained spiro-MeOTAD (S), F4-TCNQ and spiro-MeOTAD (FS), and Li-TFSI, TBP and spiro-MeOTAD (LS) were prepared. Using linear sweep voltammetry to the hole only devices, the increased slope of curve FS suggests that F4-TCNQ doping improved the conductivity of FS HTL compared with S HTL as shown in **Fig. 2 (a)**. Furthermore, the conductivity of HTL were finely measured on in-plane devices consisting of glass/HTL/Ag as H. J. Snaith proposed [28], and the electrode pattern was designed for two point probe measurements with a channel length (direction of current flow) of 2000 μm , a channel width of 2 cm and a film thickness of 500 nm was used. **Fig. 2 (b)** displays the spiro-OMeTAD conductivity (σ) as a function of the F4-TCNQ content. Generally, the pristine spiro-OMeTAD has a conductivity around 6×10^{-8} S/cm. With doping, the value of σ increases by four orders of magnitude to 1.3×10^{-4} S/cm. This can be rationalized by the fact that the hole density n increases with doping ratio (Because the doping efficiency is not 100% under all the doping ratio, so n will not increase linearly with the doping ratio), in the formula:

$$\sigma = ne\mu_h \quad (2)$$

where e is the unit of elementary charge, n is the hole density, and μ_h is the hole mobility. After reaching the maximum value, σ decreases with doping ratio, possibly because the excess F4-TCNQ⁻ act as hole-trapping-sites owing to their Coulomb potential that induce hole-electron recombination, as is widely found in the field of doped organic semiconductor system.

(**Fig. 2**)

Having understood the effect of F4-TCNQ addition on the charge transport property of

spiro-OMeTAD, we then study the effect of different doping ratio of spiro-MeOTAD with F4-TCNQ on the performance of PH PVKSCs. The solar cells were fabricated with a typical PH structure of FTO/c-TiO₂/perovskite/HTL/Ag (**Fig. 3** (a)). The perovskite CH₃NH₃PbI_{3-x}Cl_x film was deposited using a one-step solution deposition method. The cross section and the top view SEM of the perovskite solar cells are shown in **Fig. 3**. From **Fig. 3** (a, b) it can be seen that the prepared perovskite film has a very uniform thickness and high coverage, which lays the foundation for high efficient solar cell devices. **Fig. 3** (c) gives the energy levels diagram for each components of the device. **Fig. 3** (d) gives the XRD patterns of the perovskite film and its UV-Vis absorption spectrum (inset). The film grown on the FTO/c-TiO₂ substrate showed high crystallinity with high preferred orientation along the (110) direction and defined characteristic absorption spectrum of the perovskite CH₃NH₃PbI_{3-x}Cl_x crystal [29,30].

(Fig. 3)

Firstly, we studied the influence of different doping ratio of HTL on the performance of PH PVKSCs, the corresponding *J-V* curves and numerical parameters under simulated AM 1.5 G solar irradiation (100 mW/cm²) are shown in **Fig. 4** (a) and **Table 1**. In comparison to device S, increased amounts of doped F4-TCNQ in spiro-MeOTAD (devices FS1, FS1.5, and FS2.5) gave significant increases in *J*_{SC}, *V*_{OC} and FF. In particular, an enhancement of more than twice in the overall efficiency was observed in device FS1.5. These results can be attributed to the obviously increased conductivity of HTL due to the formation of spiro-MeOTAD⁺ organic cation and additional holes that resulted from the dissociation of charge transfer complex F4-TCNQ·spiro-MeOTAD. However, when the doped concentration of F4-TCNQ is high than 1.5%, the device performance decreases dramatically. This is probably because excessive doping causes excessive organic anions F4-TCNQ⁻ spatially distributed in spiro-MeOTAD film that become hole trapping traps thus reducing the conductivity and increasing the carrier recombination (**Fig. 4** (c)), as is widely demonstrated in the doped organic semiconductor system [31]. Furthermore, the doping of spiro-MeOTAD will introduce some intermediate impurity trap levels in the band gap of spiro-MeOTAD HTL. For example, supposing the HOMO level of spiro-MeOTAD does not change significantly with doping, the 525 nm absorption peak of the oxidation state spiro-MeOTAD corresponds to the transition from the trap state levels with an energy of about 0.65 eV higher than that of the HOMO level of spiro-MeOTAD. Due to the

1 amorphous character of spiro-MeOTAD film, these trap states will follow Gaussian distribution in
 2 the energy space. Anyway, the lower energy of these trap states relative to that of the conduction
 3 band of perovskite is energetically favor for electron injection into these trap states from the
 4 conduction band of perovskite (**Fig. 4 (d)**). On the one hand, such an energy-losing process can
 5 reduce the open-circuit voltage of the device. On the other hand, as electronic transmission
 6 channels, these trap states can make spiro-MeOTAD lose its electron blocking function. While the
 7 recombination of electrons and holes at the spiro-MeOTAD/Ag interface can lead to the short
 8 circuit of the device. This is consistent with the fact that the over doping leads to decreased V_{OC} ,
 9 J_{SC} and FF. The dependence of J_{SC} of the device with F4-TCNQ doped spiro-MeOTAD HTL on
 10 light densities is also investigated. As shown in **Fig. 4 (e)**, the J_{SC} is linearly proportional to light
 11 density, indicating that the charge collection efficiency in the device is independent with light
 12 power.

(Fig. 4)

(Table 1)

15 We then studied the influence of different dopant and doping ratio on the performance of PH
 16 PVKSC as shown in **Fig. 4 (b)** and **Table 1**. In comparison to device S, both devices FS and LS
 17 show increments in all performance parameters. The performance of device FS is similar to that of
 18 device LS, suggesting that F4-TCNQ doping can play the same role as Li-TFSI doping in
 19 increasing the conductivity of spiro-MeOTAD thus the final device performance. For comparison,
 20 the J - V curve of the cobalt-salt (FK209) doped device (LCS) was also given. Even with more
 21 complex doping process we did not found any significantly enhanced device performance relative
 22 to that of the LS device from our experimental results (**Table 1**). We attributed this to the complex
 23 electronic structure of spiro-MeOTAD caused by oxygen, FK209 and Li-TFSI co-doping which is
 24 not favor for charge transport. For J - V curve, the reciprocal of differential value at $J = 0$ represents
 25 the series resistance R_S of the device. Therefore R_S reflects the slope at $J = 0$ and shape of the J - V
 26 curve, and then FF was decided. Generally, the smaller R_S implies the J - V curve in the vicinity of J
 27 $= 0$ is more inclined to perpendicular to the voltage axis, which results into a larger FF. It can be
 28 calculated from **Fig. 4 (b)** that the series resistance R_S of the three devices are $7.05 \Omega \text{ cm}^2$ (LS),
 29 $13.52 \Omega \text{ cm}^2$ (FS1.5) and $19.46 \Omega \text{ cm}^2$ (S), separately. Such different R_S may result from different
 30 conductivity of different HTL due to the various dopant and doping ratio. Relative to the device S,

1 FS has a smaller R_s , and thus the FF is larger.

2 (Fig. 5)

3 To investigate the carrier transport and recombination dynamics of the device, electrochemical
4 impedance spectroscopy (EIS) measurements, as a useful characterization technique for studying
5 the interfacial charge-transfer properties of photovoltaic devices, is further carried out on the
6 devices with different HTLs. **Fig. 5 (a)** give Nyquist plots of the devices measured at the open
7 circuit potential under 1 sun AM1.5G illumination. The data in the Nyquist plot are clearly
8 separated into two distinct RC arcs. An equivalent circuit consisting of a parallel RC and $R-CPE$
9 (constant phase element) element connected in series along with an additional contribution from
10 series resistance (R_s) is employed to fit the tested data, as seen in **Fig. 5 (a)**. In the equivalent
11 circuit model, the high frequency part of the Nyquist plot is attributed to contact resistance at
12 either the ETL/perovskite or perovskite/HTL interface, whereas the lower frequency RC element
13 is associated with the recombination resistance (R_{rec}) and chemical capacitance (C_μ) of the
14 system. As the ETL/perovskite interface is identical for FS and LS device, we ascribe the higher
15 frequency feature to the contact impedance associated with the perovskite/FS HTL or
16 perovskite/LS HTL interface. **Fig. 5 (b)** displays the relationship between R_{rec} and applied bias
17 voltage for EIS measurement on the FS and LS devices. Note that, for each curve, the R_{rec}
18 decreases exponentially with the linearly increased bias voltages. The higher R_{rec} of the LS device
19 relative to that of the FS device in the applied bias voltage range indicates that more serious
20 recombination occurs at the perovskite/FS HTL interface of FS device than at the perovskite/LS
21 HTL interface of LS device, which is consistent with the photovoltaic properties of the two
22 devices as shown in **Fig. 4** and as mentioned above.

23 Recently, there have been also theoretical analysis and related experimental reports about the
24 impacts of energy level offsets at PVK/HTL interface on charge separation and device
25 performance [32-35]. Here the enhanced J_{sc} of the device FS could be related to the
26 spiro-MeOTAD contacting with F4-TCNQ by forming a charge transfer complex and then
27 dissociating into organic spiro-MeOTAD⁺ cation and F4-TCNQ⁻ anion. For pristine
28 spiro-MeOTAD, its Fermi level located at a certain position between LUMO and HOMO. Once
29 doped, the increased hole concentration led to the Fermi level moving closer towards its HOMO
30 position. The Fermi level difference between PVK and HTL increased when the spiro-MeOTAD

Fermi level moved toward its HOMO position, resulting in a larger internal electric field at the PVK/HTL interface. Therefore, the driving force of charge transfer at the PVK/HTL interface increased, resulting in an improved J_{SC} . Moreover, it is believed that spiro-MeOTAD in the PVKSCs can also absorb light contributing to J_{SC} . Here, the enhanced UV-Visible absorption of F4-TCNQ doped spiro-MeOTAD can also increase the total J_{SC} [36,37].

The enhanced V_{OC} of the device FS could be expected by deepening the HOMO of HTL[14,38]. In our case here (**Fig. 6 (a)**), the enhanced V_{OC} of the device FS can be attributed to the oxidation effect by F4-TCNQ resulting in the deepened HOMO level of spiro-MeOTAD [14,38]. As one of the most important parameters for the PVKSCs, V_{OC} was reported to be determined by the conduction band of PVK and HOMO level of HTL. However, few attentions were paid on the doping impact of the HTL properties on V_{OC} . Here, it was found that the V_{OC} will be improved with increasing the doping concentration of spiro-MeOTAD by F4-TCNQ. The V_{OC} is generally related to the turn-on voltage of the forward current under dark, which is consistent with the fact that the V_{OC} corresponds to the state where the photogenerated current is completely compensated by the dark current. Thus, a late turn-on dark current indicates a high V_{OC} . The turn-on occurred when recombination of injected carrier prevailed in the forward bias. Larger internal electric field would diminish charge recombination rate. Likewise, in our case as shown in **Fig. 6 (b)**, the turn-on point gradually moved to forward bias with the gradual doping ratio of F4-TCNQ, leading to a higher V_{OC} . In the FS1.5 device, the turn-on thresholds also moved towards forward bias, generating a larger V_{OC} .

(Fig. 6)

Finally, we compare the stability of the three kinds of devices with different HTLs, the results are shown in **Fig. 7 (a)**. The devices either S or FS retain 65-85% of the initial performance after 72 hours, and 55-60% after 7 days, respectively. While the device LS retains less than 20% of the initial performance after 72 hours, and 10-15% after 7 days, respectively. Compared with the devices either S or FS, the device LS shows a severe degradation in ambient air (humidity: 40-50%) which is attributed to the dissolving of the perovskite materials by trace amount of residue TBP and ACN as well as the decomposition of perovskite materials by the moisture attracted by hygroscopic Li-TFSI in lithium spiro-MeOTAD. We can draw the conclusion from the evolved images of perovskite films with different solvents or solutions dropped on the surface as a

function of time (**Fig. 3S and Fig. 4S**). From the experiment images, we can see that water (H_2O) will severely decompose perovskite materials as yellow lead iodide appeared instantly after a water droplet drips on the perovskite films. CB and F4-TCNQ: spiro-MeOTAD/CB solution have no significant damage to perovskite materials. DMF and TBP can easily dissolve perovskite materials, while ACN and Li-TFSI/ACN solution can dissolve and decompose perovskite materials simultaneously, judging from the appearance of pale yellow lead iodide. Thus, for stable PVKSCs, TBP, ACN, Li-TFSI and other perovskite-sensitive solvents and components should be avoided. The evolved J - V curves of the device FS as a function of time (h) are depicted in **Fig. 7 (b)**. During the investigation period, V_{OC} undergone an increase at the initial stage, probably because of the oxidation of spiro-MeOTAD by oxygen, along with a gradually decrease. While J_{SC} monotonously decreased with time due to the decomposed perovskite materials by H_2O , TBP, ACN molecules. Here we use a simple method of replacing the harmful components in the preparation of PVKSCs to enhance the device stability, further suitable encapsulation can be expected to get better stability.

(Fig. 7)

As the planar heterojunction devices can easily exhibit current hysteresis phenomenon, we tested and compared the effect of different doping on device I - V hysteresis (**Fig. 6S and Table 1S**). From **Fig. 6S and Table 1S**, the FS and LS device exhibit varying degrees of current hysteresis, which is mainly characterized by the obviously different short-circuit current density and fill factor from the forward scan and reverse scan result. To quantify the hysteresis effect, a modified I - V hysteresis index (HI) defined by eq. 1S is adopted. According to eq. 1S, the FS device gives a hysteresis index value of 0.16, while that of the LS device is 0.24. Obviously, the FS device displays slightly lower degree of hysteresis. Such a difference in the degree of hysteresis may be due to the different band bending at the interface between perovskite and hole transport layer with different doping. While, the specific mechanism needs further detailed study.

4. Conclusion

In conclusion, PH PVKSCs using F4-TCNQ doped spiro-MeOTAD as HTL presented high efficiency and substantial improved air stability. This high performance is attributed to the deeper Fermi level of p-type doped spiro-MeOTAD by F4-TCNQ. The optimized doping for p-type

doped spiro-OMeTAD was to enhance the conductivity and match the spiro-OMeTAD HOMO level with the valence band of perovskite for efficient hole extraction. The enhanced device stability originates from the replacement of hygroscopic Li-TFSI with non-hygroscopic F4-TCNQ as a hole transport layer dopant and the elimination of harmful solvents such as acetonitrile and 4-tert-butylpyridine. The effective chemical solution doping method to adjust the charge transport properties of organic semiconductor can be a promising route for fabricating highly efficient and stable PVKSCs.

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Figure captions

Fig. 1 UV-Vis absorption spectra of spiro-MeOTAD (S), mixture of spiro-MeOTAD and Li-TFSI (LS) and mixture of spiro-MeOTAD and F4-TCNQ (FS) with different molar ratio (0.5%, 1%, 1.5%, 2.5%, 3.5%) in chlorobenzene. The inset gives the images of cuvettes filled with LS, S, F, FS chlorobenzene solutions, respectively.

Fig. 2 (a) Linear J - V curves of FTO/PEDOT:PSS/HTL/Ag hole only device containing different HTL, (b) effective spiro-OMeTAD conductivity and UV-Vis absorption spectra (inset) as a function of F4-TCNQ doping ratio.

Fig. 3 (a) Cross-sectional SEM image of a PH PVKSC device based on FS HTL, (b) top view SEM image of the perovskite layer, (c) energy levels diagram for each components of the device. (d) X-ray diffraction pattern and UV-Vis absorption spectrum curve of the perovskite film.

Fig. 4 (a) J - V curves of PH PVKSCs with various composite HTLs doped by F4-TCNQ with different molar ratio, (b) J - V curves of PH PVKSCs with different dopant in HTLs, (c) schematic diagram of F4-TCNQ⁻ induced carrier recombination, (d) schematic diagram of the effect of doping induced band gap states on the electron transport process in the device and (e) plot of the J_{sc} of PH PVKSCs with F4-TCNQ doped spiro-MeOTAD HTL vs. light densities.

Fig. 5 Nyquist plots of the devices with F4-TCNQ and Li-TFSI doped hole transport layer measured at the open circuit potential under 1 sun AM1.5G illumination (a) (The inset gives the equivalent circuit model used to simulate the resultant EIS spectra), scattered point: experimental data, solid line: fitted curves; (b) Plots of R_{rec} vs. applied bias voltages for the FS and LS devices.

Fig. 6 (a) Energy band diagram at the PVK/HTL interface before and after doping by F4-TCNQ. With the p-type doping increment, the Fermi level of spiro-MeOTAD shifted downhill with the HOMO level. (b) Dark J - V curves of the devices with F4-TCNQ doped HTL with different doping ratio.

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Fig. 7 (a) Stability investigation of the unencapsulated PH PVKSCs with different HTLs, (b) *J-V* curves of the device FS under light as a function of time under the ambient air with a relative humidity of 40-50%.

1 **Table caption**

2

3 **Table 1** Performance parameters of the studied PH PVKSCs with different dopants and doping
4 ratios under 1.5 AM irradiation.

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1 **Fig. 1**

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1 **Fig. 2**

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1 **Fig. 3**

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1 **Fig. 6**

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1 **Fig. 7**

1 **Table 1**

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Devices	HTL compositions	<i>V</i> _{oc}	<i>J</i> _{sc}	FF	PCE
		(V)	(mA/cm ²)	(%)	(%)
S	pristine spiro-MeOTAD	0.761	12.67	40.16	4.08
LS	spiro-MeOTAD + Li-TFSI + TBP	0.974	19.70	64.86	12.66
FS1	spiro-MeOTAD +1% F4-TCNQ	0.832	16.41	48.62	6.99
FS1.5	spiro-MeOTAD +1.5% F4-TCNQ	0.946	18.72	56.82	10.59
FS2.5	spiro-MeOTAD +2.5% F4-TCNQ	0.903	17.35	55.02	9.07
LCS	spiro-MeOTAD + Li-TFSI + FK209+TBP	1.002	20.19	59.37	12.01

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Graphical abstract

Planar heterojunction perovskite solar cell with tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) doped spiro-MeOTAD by solvent treatment as hole transport layer was demonstrated. The device exhibits a power conversion efficiency of 10.59% and significantly improved air stability.