Fluorinated interfacial layers in perovskite solar cells: efficient enhancement of the fill factor†

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The fill factor is a key parameter in perovskite solar cells and is strongly influenced by interfacial charge transfer processes and subsequently impacts the power conversion efficiency. Herein, to improve the fill factor, three fluorine substituted materials were designed, synthesized and characterized. By inserting them as thin interfacial layers at the perovskite/spiro-OMeTAD interface, the electron blocking properties and the hole extraction and transfer efficiency were simultaneously enhanced, resulting in an enhancement of the fill factor from 75% up to ~80% while keeping the short-circuit current and the open-circuit voltage unchanged. Furthermore, the introduction of fluorine atoms increases the hydrophobicity, leading to an enhanced device stability.

Introduction

Organic–inorganic hybrid perovskites have attracted enormous attention due to their easy synthesis, high molar extinction efficiency and bi-polar charge transport.1,2 Based on these fancy materials, the development of perovskite solar cells (PSCs) is striking, with the power conversion efficiency (PCE) having increased from 3.8% in 2009 (ref. 4) to 25.2%, certified in 2019. This tremendous improvement is mainly coming from a large number of studies on perovskite active layers,6 electron transporting layers (ETLs)5 and hole transporting layers (HTLs).9

Considering the short-circuit current (Jsc), open-circuit voltage (Voc), and fill factor (FF) as the three key parameters in determining the PCE of conventional PSCs (PTO/SnO2/MAPbI3/spiro-OMeTAD/Ag), it can be seen that the Jsc is highly related to the quality of perovskite films9 and the hole mobility of the HTL, and the Voc is dependent on the energy levels between the highest occupied molecular orbital (HOMO) of spiro-OMeTAD and the Fermi level of SnO2, and the non-radiative recombination losses.10,11 The FF is the most complicated parameter to control and is strongly related to charge transfer/transport processes.12 Recently, through checking devices among high-quality PSCs (typically exhibiting a PCE over 18%), it was seen that the Jsc and Voc of these devices fluctuate in a limited range with seemingly few options for further improvement, mainly leaving more room for optimization of the FF.13

The ideal charge transport material, such as ETLs and HTLs, should have a suitable energy level, efficient charge extraction or blocking, and low surface recombination rate.14,15 Although the commonly used hole transporting material (HTM), 2,7,7′,2′-tetrakis-(N,N′-di-p-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD) shows high efficiency, it still requires additives such as LiTFSI and tBP, which would lead to electron leakage from the perovskite to the HTM,16 and stability issues. Using a dopant-free HTM strategy, Qi and co-workers reported a donor–acceptor polymer, PBT1-C, which achieved a PCE of 19.06% with a high FF of 81.22%.17 Another attempt to enhance the FF would be to decrease the interfacial losses at the interface between the perovskite active layer and the HTL or ETL.18 For example, Feng et al. inserted an ammonia modified graphene oxide (GOxNH3) layer into p-i-n PSCs and achieved an improvement of the FF from 64% to 71%.19

Herein, aiming to improve the FF of PSCs, we have designed and synthesized three carbazole-based fluorinated small molecules, F3BNCz, F5BNCz and F4BNCz2. We found that the introduction of these materials as interfacial layers into n–i–p PSCs could effectively block the electrons from passing through...
the hole transporting materials, along with forming a better contact between the perovskite and the spiro-OMeTAD layers. The FF, thereby, has been improved from 75% to ~80%, leading to an enhancement of the PCE from 18.99% to the highest 19.96%. Moreover, due to the higher hydrophobic properties of the interfacial layer, PSCs using F3BnCz, F5BnCz and F4BnCz2 showed an enhanced long-term stability over 20 days.

Results and discussion

The synthetic scheme and the chemical structure of F3BnCz, F5BnCz and F4BnCz2 are shown in Scheme 1. Details of the synthetic procedures are given in the ESI.† These three molecules have been obtained in a single step reaction by coupling 3,6-bis(4,4'-dimethoxydiphenylaminyl)-carbazole (Cz-DMPA) and commercially available fluorene derivatives.

F3BnCz has been prepared by a modified procedure reported by S. Benhattab et al.28 A Buchwald coupling of Cz-DMPA and 5-bromo-1,2,3-trifluorobenzene in the presence of Pd(OAc)2, (t-Bu)3P and t-BuONa in toluene at 110 °C allows the synthesis of F3BnCz with a yield of 62% after 6 hours. The synthesis of F5BnCz by the same procedure did not occur. Ullmann conditions using 1,2,3,4,5-pentafluoro-6-iodobenzene with K2CO3, Cu(0) and 18-crown-6 at 170 °C have already been shown in the literature,22 leading to the replacement of the iodine by a hydrogen atom. Even at low temperature (50 °C), the reaction led to N3,N3,N6,N6-tetakis(4-methoxyphenyl)-9-(2,3,5,6-tetrafluoro-4-iodophenyl)-9H-carbazole-3,6-diamine (53% yield) instead of F5BnCz. Using a nucelophilic aromatic substitution with sodium hydride,22 we could afford the target molecule. F5BnCz has been synthesized using 5 equivalents of Cz-DMPA in the presence of NaH at 0 °C (56% yield). Under the same conditions, using only 3 equivalents of Cz-DMPA at room temperature, F4BnCz2 has been obtained (80% yield). The three molecules are well soluble in common organic solvents such as toluene, dichloromethane and chlorobenzene. These fluorinated molecules have been fully characterized by 1H, 19F and 13C NMR spectroscopy and HRMS. All the analytical data are consistent with the target structures (ESI†).

The thermal properties of the three compounds have been investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (in Fig. S1, ESI†). The molecules show a high thermal stability since the decomposition temperatures are 281 °C, 265 °C and 295 °C for F3BnCz, F5BnCz and F4BnCz2, respectively. Considering the DSC measurements, it can be seen that F3BnCz and F5BnCz exhibit a molecular glass behavior with respectively a glass transition temperature of 77 °C and 44 °C. Neither crystallization nor melting transition peaks have been observed upon several heating/cooling cycles. Comparing with CzPF and CzP28 (chemical structures in Fig. S2, ESI†), it can be seen that the values of Tg are lower (82 °C for CzPF and 97 °C for CzP). The introduction of additional fluorine atoms on the benzene ring reduces the Tg. The more fluorine atoms on the benzene ring, the more the Tg decreases. These results confirm the trend that has been observed in the literature.23 For F4BnCz2, no glass transition temperature has been observed in the range of measurements (25–200 °C).

The normalized UV-Vis absorption spectra of F3BnCz, F5BnCz and F4BnCz2 in solution and as thin films are shown in Fig. 1a. In the solid state, the spectra exhibit a bathochromic shift due to π-stacking. It is noticeable that the red shift is significantly more pronounced as the number of fluorine atom increases, suggesting that the presence of fluorine atoms induces stronger intermolecular packing.28 In solution, the main peaks at 303–307 nm and 370–375 nm, which shift about 10–15 nm in solid state thin films, could be attributed to local carbazole and diphenylamine transitions. The optical band

![Scheme 1 Synthesis route and chemical structure of the interfacial molecules F3BnCz, F5BnCz and F4BnCz2](image-url)
gaps of F3BnCz and F5BnCz, as determined from the absorption onset of thin films, are similar to each other (2.75 eV). However, the introduction of a second Cz-DMPA moiety induces a decrease of 40 meV (E\text{opt} = 2.71 eV), which is characteristic of additional π–π stacking interactions and increased conjugation length.

The electrochemical properties of these glassy molecules were then studied using cyclic voltammetry (CV) in order to determine their energy levels (Fig. 1b). The three molecules exhibit two quasi-reversible oxidation waves, attributed to the formation of radical cations and dications of the carbazole moiety. The first half-wave oxidation potential is lower for F3BnCz (+0.12 V vs. Fc/Fc+) than for F5BnCz (+0.19 V). Considering the potential of the reference ferrocene/ferrocenium couple at 5.1 eV vs. vacuum, the highest occupied molecular orbital (HOMO) levels of F3BnCz and F5BnCz are determined to be 5.22 eV and 5.29 eV, respectively. As expected, the HOMO energy level is slightly lowered upon addition of strongly electronegative F atoms. F4BnCz shows a HOMO level at 5.27 eV, indicating that the grafting of a second Cz-DMPA unit does not significantly increase the HOMO level. The lowest unoccupied molecular orbital (LUMO) levels of F3BnCz, F5BnCz, and F4BnCz, extrapolated from each optical band gap, are 2.47 eV, 2.54 eV and 2.56 eV, respectively.

As shown in Fig. 1c, the HOMO energy levels of F3BnCz, F5BnCz, and F4BnCz all lie in-between MAPbI₃ (5.43 eV) and spiro-OMeTAD (5.20 eV) energy levels. Thus, all three molecules are expected to be suitable for their utilization as an interface layer, as they should allow efficient hole transfer from the perovskite films to the spiro-OMeTAD hole transporting material layer. Moreover, each LUMO level of the interfacial layers is sufficiently high to block electrons transferring from the perovskite to the spiro-OMeTAD. Hence, attempting to use these synthesized materials as interfacial materials, we have fabricated planar n–i–p type perovskite solar cells with the device configuration fluorine doped tin oxide (FTO)/SnO₂/MAPbI₃/FₓBnCz/spiro-OMeTAD/Ag (Fig. 1d). The thickness of the interfacial layer has been optimized by changing the spin speed during the spin-coating process as shown in Fig. S3 and Table S1.† It was found that at 5000 rpm, the device gives the best performance. This is possibly due to the formation of a continuous film with appropriate thickness. Devices without interfacial layers were also built and characterized as reference devices.

The current density–voltage (J–V) curves of the best-performing devices are shown in Fig. 2a, with the details of specific parameters exhibited in Table 1. The best-performing devices based on F3BnCz, F5BnCz, and F4BnCz interfacial layers obtained PCEs of 19.86% (V\text{oc} = 1.13 V, J\text{sc} = 22.10 mA cm\(^{-2}\), and FF = 79.83%), 19.86% (V\text{oc} = 1.11 V, J\text{sc} = 22.52 mA cm\(^{-2}\), and FF = 79.40%), and 19.96% (V\text{oc} = 1.12 V, J\text{sc} = 22.65 mA cm\(^{-2}\), and FF = 78.77%), respectively. For comparison, the best control device afforded a PCE of 18.99% (V\text{oc} = 1.12 V, J\text{sc} = 22.56 mA cm\(^{-2}\), and FF = 75.17%). It is noted that the interfacial layers are beneficial for the enhancement of the FF for all devices, thus leading to higher PCEs. The
corresponding external quantum efficiency (EQE) measurements were conducted as shown in Fig. 2b. The PSCs with these interfacial layers show similar EQE values around 80% in the 450 to 650 nm wavelength range, much higher than that of the control device, demonstrating the beneficial effect of the interfacial materials on the dynamics of charges. The integrated $J_{SC}$ was improved from 16.61 to $\sim 20$ mA cm$^{-2}$.

Meanwhile, Fig. 2c shows the results of steady-state current density and PCE, measured at constant bias voltages of 0.91 V, 0.94 V, 0.92 V and 0.90 V, respectively. The stabilized PCEs were 12.49%, 16.17%, 16.70% and 15.06%, with stabilized current densities of 13.73, 17.20, 18.15 and 15.06 mA cm$^{-2}$, for the devices w/o F3BnCz, F5BnCz and F4BnCz2 interfacial layers, correspondingly. This is consistent with the trend based on the parameters obtained from the $J$–$V$ curves. In addition, 20 independent devices prepared under the same conditions were fabricated, and the statistical distribution of the PCE, $V_{OC}$, $J_{SC}$ and FF is exhibited in Fig. 2d (and Fig. S4, ESI†). The PSCs with F3BnCz, F5BnCz and F4BnCz2 give a better performance than interfacial layer-free cells, with an average PCE of 18.36%, 18.26% and 18.20%, respectively, compared with only 17.19% for the reference devices. As expected, the enhancement comes from the higher FF from 72% to ca. 75–76% as indicated in Fig. S4.†

To explain the higher FF of the devices with interfacial layers, the morphology was first studied with a scanning electron microscope (SEM) as shown in Fig. 3. The MAPbI$_3$ film in Fig. 3a was highly crystallized with the crystal size ranging from 600 nm to 1 µm, with clear boundaries. From Fig. 3b–d, it can be seen that the interfacial layers basically formed a flat and homogeneous film on the perovskite. While after the deposition of spiro-OMeTAD, the morphological difference of perovskite/interfacial layer/spiro-OMeTAD (Fig. 3f–h) was even negligible. Therefore, it is considered that these comparable morphologies make no difference to the photovoltaic performance.

Table 1  Best and average photovoltaic parameters of PSCs

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{OC}$ [V]</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
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<tr>
<td></td>
<td>Best</td>
<td>Average</td>
<td>Best</td>
<td>Average</td>
</tr>
<tr>
<td>Without</td>
<td>1.12</td>
<td>1.09</td>
<td>22.56</td>
<td>21.69</td>
</tr>
<tr>
<td>F3BnCz</td>
<td>1.13</td>
<td>1.10</td>
<td>22.10</td>
<td>21.84</td>
</tr>
<tr>
<td>F5BnCz</td>
<td>1.11</td>
<td>1.10</td>
<td>22.52</td>
<td>22.07</td>
</tr>
<tr>
<td>F4BnCz2</td>
<td>1.12</td>
<td>1.11</td>
<td>22.65</td>
<td>21.62</td>
</tr>
</tbody>
</table>
To further explore the origin of the improved FF, we studied the charge transfer dynamics by conducting electrochemical impedance spectrometry (EIS) in the dark. Fig. 4a shows the Nyquist fitting results of experimental data based on various PSCs. The series resistances ($R_s$) are determined to be 13.40, 11.00, 12.05 and 10.91 $\Omega$ for PSCs with $F_3BnCz$, $F_5BnCz$ and $F_4BnCz_2$ and w/o interfacial layers, respectively. The arc can be assigned to the charge transfer process of the devices, which gives a charge transfer resistance ($R_{tr}$) of 253.14, 147.98, 167.95, and 200.09 $\Omega$, accordingly. The prominently decreased $R_s$ and $R_{tr}$ suggest a better contact at the interfaces of perovskite/interfacial layer/spiro-OMeTAD, which could favor the efficient hole transfer and transport processes and lead to an increased FF.

The charge transfer efficiency was further investigated by steady-state photoluminescence emission spectroscopy (PL) on the films of perovskite, perovskite/spiro-OMeTAD and perovskite/interfacial layer/spiro-OMeTAD on quartz, with an excitation wavelength of 450 nm. As shown in Fig. 4b, the pure perovskite film displays a strong emission peak at around 780 nm, which was significantly quenched by the deposition of spiro-OMeTAD. By comparison, upon the insertion of the interfacial layer, the photoluminescence was further suppressed, revealing the efficient extraction of photo-generated holes from the perovskite to the composite interfacial/spiro-OMeTAD hole-transporting layer. In addition, the corresponding time-resolved photoluminescence (TRPL) was examined as shown in Fig. 4c. The biexponential decay lifetime $\tau_1$, attributed to the trap-assisted recombination, is reduced from 24.71 ns to 21.53 ns after depositing spiro-OMeTAD on the perovskite film, and the values are further decreased to 4.39 ns, 12.86 ns and 18.87 ns after applying $F_3BnCz$, $F_5BnCz$ and $F_4BnCz_2$ interfacial layers between the perovskite and spiro-OMeTAD films, which demonstrates the significant suppression of traps. At the same time, the lifetime $\tau_2$, representative of free carrier recombination, is decreased from 59.97 ns to 51.02 ns, 12.70 ns, 47.50 ns, and 49.95 ns, respectively, consistent with the electron blocking effect induced by the higher LUMO levels of these interfacial materials. The details of the TRPL data and the fitting equation are shown in Table S2.†

Hence, from the EIS, PL and TRPL results, it is concluded that the insertion of these three interfacial layers could not only lead to a better interfacial contact due to the trap passivation, but also block electron back-transfer effectively due to the higher LUMO energy levels of these dopant-free interfacial layers. Thus, the insertion of our designed interfacial materials improves the charge extraction and transfer efficiency, leading to the high FF. Overall, the influence of $F_3BnCz$, $F_5BnCz$ and $F_4BnCz_2$ interfacial layers on the photovoltaic performances was quite similar.

Fig. 5 shows the stability of the PSCs with and without interfacial layers at a relative humidity around 35%. The devices with
the interfacial layers maintain 80% of the initial efficiency after 23 day storage, in sharp contrast with the SCE of the pristine device, ca. 40% of the initial PCE remains. The water-contact-angle test further confirmed the higher hydrophobicity of the fluorinated molecules, with values of $F_3BnCz$, $F_5BnCz$ and $F_4BnCz2$ of 108, 108 and 101°, respectively, which are remarkably larger than that of spiro-OMeTAD (85°). Hence, the fluorinesubstituted interfacial layers are more water-resistant and protect the perovskite from moisture efficiently. The thermal stability of the solar cells has also been investigated as shown in Fig. S5.† After the continuous thermal annealing of the devices at 85 °C, the devices with interfacial layers show a better PCE stability than the interfacial layer free device.

**Conclusions**

In summary, aiming at the enhancement of the FF, we have designed and synthesized a series of novel fluorinated small molecules as interfacial layer materials to improve the contact between the perovskite and spiro-OMeTAD. Through the investigation of their optical, electrochemical and photovoltaic properties, we found that the influence of the small variation on the molecular structure, such as the number of F atoms or the dimer derivative, is highly limited. Finally, the perovskite solar cells with these interfacial layers show a better PCE owing to a significant increase of the FF, up to ~80% based on the MAPbI$_3$ system, while maintaining $J_{sc}$ and $V_{oc}$ unchanged. Furthermore, the device stability has also been improved due to their stronger hydrophobicity.

**Author contributions**

R. W. conducted the device fabrication and characterization. R. N. designed and synthesized the molecules. R. W., R. N., Y. J. and J. W. G. wrote the manuscript. All the authors discussed the results and made contributions to the manuscript. J. W. G. directed the research.

**Conflicts of interest**

There are no conflicts to declare.

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