Molecule-Doped Nickel Oxide: Verified Charge Transfer and Planar Inverted Mixed Cation Perovskite Solar Cell

Wei Chen, Yecheng Zhou, Linjing Wang, Yinghui Wu, Bao Tu, Binbin Yu, Fangzhou Liu, Ho-Won Tam, Gan Wang, Aleksandra B. Djurišić,* Li Huang,* and Zhubing He*

Both conductivity and mobility are essential to charge transfer by carrier transport layers (CTLs) in perovskite solar cells (PSCs). The defects derived from generally used ionic doping method lead to the degradation of carrier mobility and parasite recombinations. In this work, a novel molecular doping of NiO hole transport layer (HTL) is realized successfully by 2,2′-(perfluoronaphthalene-2,6-diylidene)dimalononitrile (F6TCNNQ). Determined by X-ray photoelectron spectroscopy and ultraviolet photoelectron spectroscopy, the Fermi level ($E_F$) of NiO, HTLs is increased from $-4.63$ to $-5.07$ eV and valence band maximum (VBM)-$E_F$ declines from $0.58$ to $0.29$ eV after F6TCNNQ doping. The energy level offset between the VBMs of NiO, perovskites declines from $0.18$ to $0.04$ eV. Combining with first-principle calculations, electrostatic force microscopy is applied for the first time to verify direct electron transfer from NiO, to F6TCNNQ. The average power conversion efficiency of CsFAMA mixed cation PSCs is boosted by $8\%$ depending on F6TCNNQ-doped NiOx HTLs. Strikingly, the champion cell conversion efficiency of CsFAMA mixed cations and MAPbI$_3$-based devices gets to $20.86\%$ and $19.75\%$, respectively. Different from passivation effect, the results offer an extremely promising molecular doping method for inorganic CTLs in PSCs. This methodology definitely paves a novel way to modulate the doping in hybrid electronics more than perovskite and organic solar cells.

Intensive research into organometallic halide perovskite solar cells (PSCs) has led to the shift from pure methylammonium (MA) to formamidinium (FA)-based mixed cation perovskites$^{1–11}$ with the record power conversion efficiency (PCE) as high as over 22%. Mixing organic cations with small amounts of Cs$^+$ or Rb$^+$ cations leads to a more favorable tolerance factor that facilitates the stabilization of the photoactive perovskite phase in a broader temperature range$^{13}$ and results in their high thermal and environmental stability in over 1000 h of light soaking.$^{7,11,14,15}$ It is a crucial criterion for PSCs to scale up in the future commercialization.

Among all the kinds of PSC device structures, the planar heterojunction, especially the planar inverted device, has attracted extensive attention of researchers owing to its simpler device architecture and more facile fabrication. NiO$_x$ nanocrystal film is an excellent choice as hole transport layers (HTLs) in such device structure.$^{16,17}$ Because the valence band maximum (VBM) of NiO$_x$ matches well with that of mixed cation perovskites while its conduction band minimum (CBM) is much higher than that of the perovskite materials. This ensures the maximum photocurrent and minimum voltage losses of NiO-based PSCs.$^{18–21}$ Although intrinsic NiO shows a p-type semiconductor$^{22}$ with high hole mobility,$^{23}$ its major carrier (hole) concentration is low and the Fermi level is far from its VBM, which results in weak built-in field strength in a limited film thickness and large energy level offset at the NiO–perovskite interface.$^{24}$ Derived from that, the low holes transfer efficiency of intrinsic NiO would result in hole accumulation near the perovskite interface and hence large possibility of electron–hole recombination at the NiO–perovskite interface.$^{20,25–27}$ For this concern, considerable efforts have been successfully made to enhance p-type doping of NiO and hence to improve band alignment at the NiO–perovskite interface by ionic doping of a thin layer of NiO nanocrystal films.$^{26–28}$ Ideally, this doped NiO layer should be uniform, dense, and 10–20 nm thick, which is a challenge.$^{29}$ The ionic doping in NiO lattice definitely creates considerable crystal lattice disorder and defects, hence causing the degradation of carrier mobility and parasite recombination, which demands the HTL thickness should be thin enough.$^{15}$ As a result, there is always a trade-off between carrier concentration and mobility in almost all the semiconductors when doping. The perfect state is to possess both high mobility and...
high conductivity at the NiO$_x$-perovskite interface simultaneously. Moreover, the doping definitely complicates the fabrication procedure, shrinks its process window, and raises the cost.

On the other hand, doping of semiconductors by organic molecules is attracting more and more attention of researchers in hybrid electronics.$^{[29–41]}$ Molecular p- or n-doping of colloid quantum dots (QDs) and 2D semiconductors have also been demonstrated to improving the device performance of QD solar cell and increasing the field effect mobility of 2D semiconductors.$^{[30,32]}$ In term of NiO, such phosphonic acid contained organic molecules as alkylphosphonic acid,$^{[42]}$ phosphonic acid,$^{[43,44]}$ and 4-cyanophenylphosphonic acid$^{[45]}$ were used to modulate the work function of NiO by means of charge transfer between the hydroxylated NiO surface and the phosphonate groups. However, this is not a good choice for PSCs due to the yielded NiOOH interlayer, indefinite charge transfer direction, and high possibility of undesired recombination. For NiO-based PSCs, diethanolamine (DEA) was used to improve the crystalline quality of MAPbI$_3$Cl$_x$ perovskite film and to passivate surface defects of NiO, resulting in an enhanced device performance of near 16% in PCE.$^{[46]}$ Combining the DEA passivation of NiO$_x$ surface with interface engineering at the cathode side, PCE as high as 18.1% was obtained for MAPbI$_3$-based PSCs.$^{[47]}$ However, in both works, DEA plays a role as passivating agent other than molecular doping for NiO. Therefore, it is of great interest to investigate the mechanism of p-type doping of NiO by robust molecules with a facile modification process compatible with the fabrication of PSCs.

In this work, a robust p-type molecular dopant, 2,2’-(per-fluoronaphthalene-2,6-diylidene) dimalononitrile (F6TCNNQ), was successfully employed to modulate the p-type doping of NiO$_x$ HTLs in PSCs. F6TCNNQ is a strong electron-acceptor molecule and low LUMO energy level ($\approx$5.37 eV) of the molecular dopant$^{[31,40]}$ matches well with the VBM ($\approx$5.2 eV) of NiO$_x$. Combining theoretical calculation and experimental characterization results, F6TCNNQ was discovered as an effective p-type molecular dopant to increase both NiO and F6TCNNQ HTLs, and as upgrading the conductivity of NiO$_x$ film by increasing hole concentration inside. This results in the reduction of energy level offset between NiO$_x$ and perovskites, which remarkably enhances holes extraction efficiency and reduces the contact resistance at the NiO$_x$-perovskite interface. Based on that understanding, F6TCNNQ-doped NiO$_x$ boosts the inverted planar MAPbI$_3$-based best devices performance to nearly 20% in PCE, as compared to the controlled one with the bare NiO$_x$ (18.19%). Strikingly, using Cs$^+$, HC(NH$_2$)$_2^+$ and CH$_2$NH$_2^+$ (CsFAMA) mixed cations perovskites with broader photon absorption, the best devices performance was enhanced from 19.6 to 20.86%, which is comparable to latest reported efficiencies of the inverted planar PSCs.$^{[38]}$

The NiO$_x$ HTLs were deposited on cleaned ITO glass with NiO$_x$ nanoparticle inks at room temperature according to previously reported procedure.$^{[18,49]}$ Obtained NiO$_x$ thin films were uniform and pinhole free.$^{[18,49,50]}$ Chemical structure of molecular dopant F6TCNNQ is shown at Figure 1a. It is composed of six fluorine substitutes on naphthalene core and four cyano functional groups, hence it can be easily ionized by attracting electrons.$^{[31,36,40,41]}$ The reason that we select this dopant is its high EA and significant low uncouparated molecular orbital (LUMO) energy level ($\approx$5.37 eV)$^{[31]}$ which is $\approx$0.16 eV lower compared to the VBM of NiO$_x$ (5.21 eV) (Figure 1a). The molecular doping was simply achieved by loading and spin coating the acetonitrile (ACN) solution of F6TCNNQ onto as-prepared NiO$_x$ thin films, followed by annealing at 80 °C overnight (see more details in ESI). Based on the anticipated effect of molecular doping of NiO$_x$ HTLs by F6TCNNQ, planar-inverted MAPbI$_3$ PSCs with and without the molecular doping of NiO$_x$ HTLs were investigated. Device structure is depicted in Figure S1a in the Supporting Information. Perovskite active layers were deposited with previously reported one-step antisolvent method (see more details in ESI).$^{[51]}$ PC$_{61}$BM and ZrAcac are selected as electron transport layer (ETL) and cathode interfacial layer (CIL).$^{[18,27,52]}$ The current–voltage (I–V) curves of the PSCs with pristine and p-doped NiO$_x$ HTLs were shown in Figure S1 in the Supporting Information, and summarized in Table S1 in the Supporting Information. The best device efficiency of the PSCs with the p-doped NiO$_x$ achieved a PCE of 19.75% with open circuit voltage ($V_{oc}$) of 1.12 V, short-circuit current density ($J_{sc}$) of 22.05 mA cm$^{-2}$, and fill factor (FF) of 80.0%. All the three device parameters are obviously augmented in contrast to the best control device with a PCE of 18.19%. Both control and p-doped devices exhibit negligible hysteresis effect, which shows high device quality and is consistent with observations in previous reports (Figure S1c,d, Supporting Information).$^{[19,53]}$ The optimal device performance is obtained with modification of an F6TCNNQ solution of 10 $\times$ 10$^{-3}$ mg mL$^{-1}$, which will be used for following discussions (Figure S1b, Supporting Information).

To figure out the mechanism behind the improvement, electronic structures of NiO$_x$ with and without F6TCNNQ doping were probed with ultraviolet photoelectron spectroscopy (UPS), which is widely used to study the density of states below the Fermi level ($E_F$) of a material and its surface.$^{[36–38,39,40]}$ As shown in Figure 1b,c, the valance band spectra show that the energetic gap between $E_F$ and $E_F$ of NiO$_x$ becomes narrow from 0.58 to 0.29 eV after F6TCNNQ doping and also indicates that its hole concentration increases too. From the UPS measurement, we can directly determine the work functions (WF) of the pristine and molecule-doped NiO$_x$ thin films, which are $\approx$4.63 to $\approx$5.07 eV, respectively (Figure 1c). The VBM levels of the pristine and doped NiO$_x$ were calculated to be $\approx$5.21 and $\approx$5.36 eV, respectively. This indicates successful electron transfer from NiO$_x$ to F6TCNNQ, which is consistent to some previous reports of F6TCNNQ and related compounds.$^{[36,40,41,45]}$

All the values are approaching that of the perovskites, which definitely narrows the energy level offset for hole transfer between NiO$_x$ and the perovskites and improves the device performance. From X-ray photoelectron spectroscopy (XPS) measurements, the Ni 2p core level peak has an unambiguous shift of $\approx$0.17 eV after the doping of F6TCNNQ (Figure 1d), which further convinces us of electron transfer occurred and agrees with the phenomena of a shift of the Mo core level peak in molecular-doped 2D MoS$_2$.$^{[12]}$ No additional or new chemical components were detected by the XPS except the F and N signals from the molecular dopant, indicating the successful doping of NiO$_x$ films (Figure S2, Supporting Information). Based on these data, the schematic band diagrams of the NiO$_x$–perovskite interface in the PSCs were illustrated in Figure 1e, where the VBM and $E_F$ of MAPbI$_3$ perovskites are set at 5.4 eV and at
the middle of the band gap, respectively. It is clearly shown that the energy level offset ($\Delta E$) for charge transfer between the VBMs of NiO$_x$ and perovskite is reduced from initial 0.18 eV to as low as 0.04 eV, which is of paramount interest to the enhancement of the devices’ open-circuit voltage and other performance owing to suppressing thermionic losses. Owing to the simultaneous reduction of its work function, the band bending of NiO$_x$–perovskite interface was enlarged from 0.03 to 0.47 eV. As the band bending becomes deeper, F6TCNNQ-dominated interface has lower holes concentration in the superficial space charge region of NiO$_x$, resulting in more efficient charge transport from perovskites (Figure 1f).

Moreover, the conductivities of NiO$_x$ before and after molecular doping have been measured by $I$–$V$ scan. The $I$–$V$ profiles of the pristine and F6TCNNQ-doped NiO$_x$ thin films on Al$_2$O$_3$ substrates with Au interdigitated electrodes showed significant enhancement in conductivity after doping (Figure S3, Supporting Information). The results indicate that (1) the conductivity enhancement is remarkable with at least 1 order of magnitude and (2) the ionization of F6TCNNQ is uniform across the whole surface. This further convinces us that the modification of F6TCNNQ on NiO$_x$ is uniform, robust, and reproducible, which affords huge potential in its application in hybrid electronics.

Although all the above evidences support convincingly the electron transfer from NiO$_x$ HTLs to F6TCNNQ that contributes to the device performance enhancement tested above, they are not direct. Therefore, to further confirm our results, theoretical calculations were performed with first-principle simulations to investigate the doping mechanism in the molecular p-doping of NiO$_x$. The frontier orbital energy levels of the F6TCNNQ molecule were calculated by Gaussian 09 1A under the level of B3LYP/6-311g* (Figure S5, Supporting Information). The LUMO and highest occupied molecular orbital (HOMO) of F6TCNNQ are calculated at $-5.56$ and $-7.44$ eV, respectively. It is previously discovered that the relationship between conductivity enhancement and morphology evolution in F4TCNQ-doped quartenithiophene. Here, conductive AFM (c-AFM) was directly applied to investigate their microscopic conductivity variation before and after doping (Figure S4, Supporting Information). The results indicate that (1) the conductivity enhancement is remarkable with at least 1 order of magnitude and (2) the ionization of F6TCNNQ is uniform across the whole surface. This further convinces us that the modification of F6TCNNQ on NiO$_x$ is uniform, robust, and reproducible, which affords huge potential in its application in hybrid electronics.

Figure 1. a) Band alignment of NiO$_x$ and molecular dopants of F6TCNNQ and the chemical structure; b) Valance band spectra of the NiO$_x$ and F6TCNNQ-doped NiO$_x$; c) UPS spectra of the NiO$_x$ and F6TCNNQ-doped NiO$_x$ measured under $-10$ V bias. The work function are calculated with equation $\phi = h\nu - (E_F - E_{F(Au)})$, where the $E_{F(Au)}$ is the Fermi level of reference Au under $-10$ V bias; c) High-resolution XPS spectra of Ni for the pristine and F6TCNNQ-doped NiO$_x$; the core level of Ni 2p$_{3/2}$ shifted $+0.17$ eV after molecular p-doping; e,f) Impact of molecular doping of F6TCNNQ on the band bending at p-type doped NiO$_x$–perovskite interface. $E_F$ of the doped NiO$_x$ (e) is closer to the valence band maximum (VBM) of the pristine NiO$_x$ (f). The work function $\phi$ of the pristine NiO$_x$ increases from 4.63 to 5.07 eV upon treatment with the p-type molecular dopant. The VBM of the doped NiO$_x$ (5.36 eV) went deeper than pristine NiO$_x$ (5.21 eV) as referred to vacuum level. The energy level offset between the VBM of NiO$_x$ and perovskite decreased from 0.18 eV for pristine NiO$_x$ to 0.04 eV for p-doped NiO$_x$, indicating more efficient charge transfer at the molecular p-doped NiO$_x$–perovskite interface.
respectively, which agree with experiments and theory reported by Karpov et al. These deep LUMO and HOMO suggest the high electron affinity (EA) energy, which measures the ability of electron attracting. As expected, the adiabatic EA was calculated to be $-4.28$ eV, which is higher than the highest element EA (fluorine, $-3.4$ eV). The high EA suggests that F6TCNNQ can harvest electrons from the host and p-type dope host. A successful molecule doping of NiO also requires that the molecule could be adsorbed and hold steady on NiO surface. To clarify the doping and charge transfer processes, we built a model of an F6TCNNQ molecule on an O-terminated NiO$_{x}$ 100 surface, as shown in Figure 2a. An F6TCNNQ molecule was put on a 5 $\times$ 5 [100] NiO surface with lattice parameters of 14.53 Å $\times$ 14.53 Å. The adsorption calculations of the adsorption model were performed using VASP 5.4 with PBE exchange-correlation function. All structures were relaxed until the force on every ion is smaller than 50 meV Å$^{-1}$. The adsorption energy is defined by $E_{\text{adsorption}} = E_{\text{NiO+F6TCNNQ}} - E_{\text{NiO}} - E_{\text{F6TCNNQ}}$, where $E_{\text{NiO+F6TCNNQ}}$ is the total energy of the molecule adsorbed on the [100] NiO surface and $E_{\text{NiO}}$ and $E_{\text{F6TCNNQ}}$ are the total energies of the [100] NiO surface and the F6TCNNQ molecule, respectively. After geometry relaxation, the distance between F6TCNNQ conjugated plane and the outmost O atoms plane of NiO$_{x}$ is 3.1 Å. The strong interaction between of F6TCNNQ and NiO$_{x}$ reshapes the NiO$_{x}$ surface: O atoms under F6TCNNQ sink about 0.3 Å, as shown in Figure 2b. The adsorption energy was calculated to be 0.43 eV, which indicates very strong adsorption. Charge density difference ($\rho_{\text{NiO+F6TCNNQ}} - \rho_{\text{NiO}} - \rho_{\text{F6TCNNQ}}$) of this model was calculated, which is shown in Figure 2c. It is clear that the electron density of the molecule becomes higher, while electron density of NiO$_{x}$ layer becomes less. Additionally, the harvested electrons are mainly localized on the F and N elements. This elucidates that it is possible to realize strong p-type by introducing strong electron withdrawing elements or groups. By performing a Bader charge analysis on this adsorption model, we find indeed there is 0.07 e transferred from NiO$_{x}$ layer to an F6TCNNQ molecule. Generally, our first-principle calculations show that (1) F6TCNNQ can be strongly absorbed by NiO$_{x}$ layer and (2) electrons will transfer from NiO$_{x}$ layer to F6TCNNQ and then realize p-type doping of NiO$_{x}$.

We also used electrostatic force microscopy (EFM) to examine directly the charge transfer between F6TCNNQ and NiO$_{x}$ and to investigate the above simulation results. In fact, EFM can offer direct information of relative charge concentration and types, and even imaging. It was already successfully applied to quantitatively estimate carrier density and type in P3HT and pentacene nanostructures, CdSe@ZnS quantum dots, etc. In this work, to prepare standard EFM...
samples, NiO$_x$, F6TCNNQ, and F6TCNNQ/NiO$_x$ were spin coated on bare insulating glass substrates. Figure 3a illustrates the testing scheme of EFM, where the bias voltage (−9 to 9 V with a step of 3 V) applied on the tip to allow extraction of the Coulombic forces. Figure 3b–d shows phase shift mapping across the whole scan region at different bias voltages integrated in one image for comparison. For crystalline NiO$_x$ films, the phase shift mapping has enough space resolution that grains and grain boundaries in the film can be clearly discerned (Figure 3b,c), while noncrystalline F6TCNNQ thin film cannot (Figure 3c,d). Most importantly, the phase shift degree for each kind of films is easily distinguished, which is summarized in Figure 3e. On the platform of the Asylum Research MFP-3D, the negative shift of the symmetry axis of the fitting parabola denotes negative charges induced at the surface point or area, and vice versa. The fit curve of the bare NiO$_x$ film (black) on glass substrate shows its symmetrical axis is around the bias voltage of 0 V, which claims very low charge concentration induced. For the bare F6TCNNQ thin layer, a small amount of negative charges can be detected as the blue dash line shown, which can be attributed to that some F6TCNNQ molecules are already ionized by environmental factors owing to its high electron affinity. For F6TCNNQ-modifying NiO$_x$, the number of negative charges remarkably increases in contrast to both of them separately, which definitely demonstrates that considerable electrons are transferred from NiO$_x$ to ionize F6TCNNQ molecules. So, EFM provides us an alternative powerful tool to discover direct charge transfer in molecular doping of NiO$_x$.

To obtain high performance PSCs, FA, MA, and Cs mixed perovskite instead of MAPbI$_3$ are more commonly employed as active layers in PSCs due to the broader photon absorption and higher thermal and environmental stabilities. Through tailoring the stoichiometric ratio of different cations and lead anion in the precursor solution, high-quality perovskite films can be deposited to achieve device efficiency over 21%. Keeping this in mind, it is of great interest to further investigate the effect of molecule-doped NiO$_x$ HTLs for CsFAMA mixed cation PSCs. The CsFAMA mixed perovskites were deposited with similar procedures as MAPbI$_3$ except for the precursor solution preparation (see more details in ESI). The as-prepared mixed perovskite films on both NiO$_x$ and F6TCNNQ-doped NiO$_x$ HTLs exhibit similar morphology, as demonstrated by scanning electron microscopy (SEM) and AFM (Figure 4a, Supporting Information), indicating negligible influence of molecular dopant on perovskite morphology. Figure 4a,b shows dense and uniform cross-section morphologies of CsFAMA perovskite films composed of large crystalline grains deposited on both kinds of HTLs, which benefits suppressed defect state density and enhanced carrier transport properties. Due to space resolution limitation of the SEM, it is hard to define the nanoscale information of the NiO$_x$ HTLs before and after molecular doping. Thus, we use a more sophisticated scanning transmission electron microscopy (STEM) to explore the cross-section information of our devices at high resolution. As shown in Figure 4c,d, each layer in both pristine and doped NiO$_x$ devices can be clearly distinguished from the cross-section STEMs. Elemental mapping demonstrates uniform distributions of Cs and Pb in CsFAMA perovskite films, implying the successful incorporation of Cs$^+$ into the mixed cation perovskite films. Ni signal is shown in the two corresponding images. Due to the influence of neighbor elements,
the signal of fluorine has considerable noise background. However, it is clear that F signal in the F6TCNNQ-doped NiO$_x$ layer is apparently brighter than in the pristine NiO$_x$. To further determine the actual F6TCNNQ molecular dopant distributions across the NiO$_x$ layer and/or at the NiO$_x$–perovskite interfaces of the samples without ETLs and electrodes, the distribution of fluorine throughout the doped NiO$_x$ layers was investigated by time-of-flight secondary ion mass spectrometry (ToF-SIMS) elemental depth profiling (Figure 4e,f). Both F$^-$ and Ni$^+$ signals increase after perovskite layer, but F$^-$ signal is higher than Ni$^+$ at the interface between NiO$_x$ and perovskite. Along with a 3D overlayer mode of ToF-SIMS results (Figure S7, Supporting Information), it is indicated that the molecular dopants indeed penetrated into the grain boundaries of NiO$_x$ nanocrystal layer, which guarantees strong p-type doping effect and the improvement of devices performance.

Moreover, charge transfer dynamic at pristine and doped NiO$_x$–perovskite interfaces were probed with steady and time resolved photoluminescence (PL). The PL intensity for perovskites on NiO$_x$ HTL is significantly quenched compared to perovskite on indium doped tin oxide (ITO) substrate due to the transfer of photon-excited carriers from perovskite to NiO$_x$ (Figure S8a, Supporting Information). After molecular doping of NiO$_x$, more efficient charge transfer can be realized, which causes stronger quenching of PL intensity for perovskite on doped NO$_x$ (Figure S8a, Supporting Information). This can be confirmed by the shorter PL lifetime of the perovskite on the doped NiO$_x$ than that on the undoped one (Figure S8b and Table S1, Supporting Information). These results demonstrate again that the molecular doping of NiO$_x$ HTL could significantly enhance the charge transfer efficiency at NiO$_x$–perovskite interface and improve the final device performances.

Photovoltaic performances of the CsFAMA perovskite PSCs with pristine and molecule-doped NiO$_x$ HTLs were comprehensively investigated and analyzed, as presented in Figure 5. $I$–$V$ curves of the optimal devices based on both the pristine and the doped NiO$_x$ HTLs demonstrate the performance can also be remarkably improved by F6TCNNQ-doped NiO$_x$ HTLs (Figure 5a). The champion cell with the optimal PCE of 20.86% has been achieved while the controlled device without doping obtained a best PCE of 19.69%. Compared with MAPbI$_3$-based
devices, the improvement of CsFAMA mixed cations perovskite devices comes mainly from the increase of $J_{sc}$, which is attributed to the broader solar spectrum absorption of CsFAMA perovskite film. In Figure 5b,c, both of those optimal devices exhibit negligible hysteresis behavior similar to the MAPbI$_3$ devices (Figure S1, Supporting Information), which further demonstrates excellent carrier transport at both anode and cathode sides. All the photovoltaic parameters are summarized in Table 1. Furthermore, steady power output (SPO) tests were recorded to further confirm negligible hysteresis of the corresponding devices. Figure 5d showed the steady photocurrent profiles as long as 300 s under a fixed bias at the maximum power point. It is obvious that the photocurrent densities of both devices stay almost constant with the time. The SPO efficiencies are 20.56 and 19.32% for the optimal devices with doped and undoped NiO$_x$, respectively, which are comparable to the PCE obtained from $I$–$V$ curves.

Finally, external quantum efficiency (EQE) is employed to explore the photon to current conversion efficiency. The EQE spectra covered the entire visible range from 300 to 800 nm with averaged EQE over 85% for both doped and controlled devices (Figure 5e). As expected, the device with doped NiO$_x$ showed higher EQE than control devices, especially at long wavelength (700–800 nm), which is attributed to probably the enhanced charge transfer and more balanced photocurrent collection efficiency in the molecule-doped NiO$_x$-based devices[66,67] and also might be favored by the modulated electronic structures at FTCNNQ and perovskite interfacial layer[39,40].

$J_{sc}$ calculated from the integration of EQE spectra are 22.45 and 21.99 mA cm$^{-2}$ for molecule-doped NiO$_x$ and control devices, respectively. Both values are within the reasonable error range and well matched with the values from $I$–$V$ measurements[18,19]. The statistics of performances for total 32 devices were presented in Figure 5f and Figure S9 in the Supporting Information and summarized in Table 1. As we can see that the averaged PCE for control devices is 18.70%, which is ≈7% less than that for devices with F6TCNNQ-doped NiO$_x$ (19.96%). From the statistics, the main improvement originated from the $V_{oc}$, from 1.06 to 1.1 V (Figure S9, Supporting Information). Moreover, the series resistance is decreased, while

**Table 1.** Summary of photovoltaic parameters of inverted PSCs with CsFAMA perovskite based on pristine and molecular $p$-doped NiO$_x$ HTLs.

<table>
<thead>
<tr>
<th>Devices</th>
<th>Scan direction</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>$J_{sc}$ by EQE [mA cm$^{-2}$]</th>
<th>$V_{oc}$ [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
<th>$R_s$ [Ω cm$^{-2}$]</th>
<th>$R_{sh}$ [kΩ cm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO$_x$</td>
<td>Reverse</td>
<td>22.46 ± 0.16$^a$ (22.74)$^b$</td>
<td>21.99</td>
<td>1.06 ± 0.016 (1.09)</td>
<td>76.0 ± 1.6 (79.6)</td>
<td>18.70 ± 0.52 (19.69)</td>
<td>2.6</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>Forward</td>
<td>22.71</td>
<td>1.08</td>
<td>79.7</td>
<td>19.61</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecule-doped NiO$_x$</td>
<td>Reverse</td>
<td>22.90 ± 0.14 (23.18)</td>
<td>22.45</td>
<td>1.10 ± 0.017 (1.12)</td>
<td>77.8 ± 1.7 (80.3)</td>
<td>19.96 ± 0.61 (20.86)</td>
<td>1.9</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>Forward</td>
<td>23.15</td>
<td>1.12</td>
<td>80.2</td>
<td>20.81</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$The averaged values of 32 devices from different batches; $^b$In the parenthesis are the values corresponding to the best devices.
the shunt resistance is increased after F6TCNNQ doping of NiO\textsubscript{x} HTLs (Table 1). The improvements of both $V_{oc}$ and FF mean the F6TCNNQ doping of NiO\textsubscript{x} decreases effectively the recombination at the NiO\textsubscript{x}–perovskite interface along with the enhancement of carrier transport.

In summary, we have demonstrated a novel strategy to tailor the optoelectronic properties of inorganic hole transporting layer in perovskite solar cells. Through a simple solution based on one-step method, NiO\textsubscript{x} HTLs can be strongly p-type doped with F6TCNNQ molecules. Along with XPS, UPS was employed to define the increase of work function and VBM of NiO\textsubscript{x} HTLs after doping with F6TCNNQ. The energy level offset for charge transfer between the VBMs of NiO\textsubscript{x} and perovskite is reduced from 0.18 to 0.04 eV. Combining with first-principle calculations, EFM was applied to directly verify electron transfer from F6TCNNQ to NiO\textsubscript{x} confirming the above conclusion as well as the increase of holes concentration and narrowing of VBM-E\textsubscript{F} of NiO\textsubscript{x}. As a result of this, the average PCE of CsFAMA mixed cation PSCs was boosted by ≈7% for F6TCNNQ-doped NiO\textsubscript{x} HTLs. The champion cells for the CsFAMA mixed cation and MAPb\textsubscript{I} perovskite exhibited PCE of 20.86% and 19.75%, respectively. Thus, our results offer an extremely promising molecular doping method for inorganic carrier transport layers in PSCs, which can potentially be extended to other combinations of inorganic semiconductors and functional organic molecule dopants in the future. This methodology paves a novel way to modulate the doping in hybrid electronics more than perovskite and organic solar cells.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

W.C. and Y.C.Z. contributed equally to this work. The authors thank Materials Characterization and Preparation Center (MCPC) and the Pico Center of SUSTech for some characterizations in this work. This work was supported by the National Natural Science Foundation of China (NSFC) (Nos. 61775091 and 11774142), the National Key Research Project MOST (No. 2016YFA0202400), Natural Science Foundation of Shenzhen Innovation Committee (No. JCYJ20150529152146471), and the Shenzhen Key Laboratory Project (No. ZDSYS201602261933302).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

2,2$′$-(perfluoronaphthalene-2,6-diylidene)dimalononitrile (F6TCNNQ), CsFAMA mixed cations perovskite, electrostatic force microscopy (EFM), molecular doping, NiO

Received: January 23, 2018
Revised: February 14, 2018
Published online: 1800515
