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## High-Performance and Low-Hysteresis Lead Halide Perovskite Solar Cells by Utilizing a Versatile Alcohol-Soluble Bispyridinium Salt as an Efficient Cathode Modifier

Guiting Chen,<sup>†</sup><sup>a</sup> Fan Zhang,<sup>†</sup><sup>b</sup> Meiyue Liu,<sup>a</sup> Jun Song,<sup>\*b</sup> Jiarong Lian,<sup>b</sup> Pengju Zeng,<sup>b</sup> Hin-Lap Yip,<sup>\*a</sup> Wei Yang,<sup>a</sup> Bin Zhang<sup>\*ab</sup> and Yong Cao<sup>a</sup>

A novel alcohol-soluble conjugated bispyridinium salt (**FPyBr**) is developed and used as a cathode modifier to improve the cathode interface of planar heterojunction perovskite solar cells (PHJ PVSCs). The excellent electron-withdrawing ability of bispyridinium rings endows **FPyBr** with a favorable energy level alignment with phenyl-C<sub>60</sub>-butyric acid methyl ester (PCBM) and the cathode (e.g., Al), which leads to an ideal ohmic contact and efficient electron transport and collection. The deep-lying highest occupied molecular orbital energy level of **FPyBr** can also effectively block hole carriers and thus decreases leakage current and hole-electron recombination at the cathode interface. In addition, **FPyBr** can n-dope PCBM through an anion-induced electron transfer process, which increases the electron mobility of PCBM drastically, thereby diminishing interfacial resistance and promoting electron transport. As a result, by incorporating a **FPyBr** cathode interlayer with ethanol solvent, high-performance and low-hysteresis PHJ PVSCs with a maximal power conversion efficiency (PCE) of 19.61% can be realized. On the contrary, the reference devices without any cathode interlayer display a distinctly worse performance, with a PCE of 16.97%. Therefore, this excellent cathode modifier provides a new opportunity to fabricate high performance multilayer PVSCs using low-temperature solution processing without interfacial erosion/mixing.

#### Introduction

Organic-inorganic hybrid perovskite solar cells (PVSCs) have attracted significant attention due to their unique advantages,<sup>1-4</sup> including light weight, low-cost solution processability, mechanical flexibility and high efficiency close to traditional solar cell technologies, such as crystalline silicon, copper indium gallium selenide/sulfide and cadmium telluride.<sup>5</sup> Since perovskite semiconductors possess excellent optoelectronic properties,<sup>6-8</sup> including tunable band gaps, high absorption coefficients, long exciton and charge carrier diffusion lengths and lifetimes, low exciton binding energies and ambipolar charge transport, the performance of PVSCs has been improved drastically in a short time and the power conversion efficiency (PCE) values have already surpassed 20%.<sup>5,9-11</sup>

Generally, the device configurations of PVSCs can be

(regular and inverted) structures.<sup>12,13</sup> As the device fabrications mesoporous architectures usually involve hightemperature (> 450 °C) sintering processes for TiO<sub>2</sub> scaffolds, which increase the cost and are incompatible with flexible substrates, PHJ structures are therefore considered to be more desirable for the realization of the large-scale production of flexible devices using a continuous and cost-effective solutionprinting process.<sup>14</sup> Alternatively, although regular PVSCs have shown slightly higher PCEs than the inverted ones, photocurrent hysteresis was found to be more serious for regular PVSCs. Indeed, inverted PVSCs often display lower hysteresis that is attributed to the better passivation of electronic trap states at the perovskite/electron transporting layer (ETL) interface by electron transporting materials (ETMs) (e.g., fullerene derivatives).<sup>4</sup> Therefore, it is urgent to improve the PCEs of inverted PHJ PVSCs in order to obtain highperformance PVSCs with negligible hysteresis.

classified as mesoporous and planar heterojunction (PHJ)

One of the most commonly used device architectures for inverted PHJ PVSCs is ITO/poly(3,4ethylenedioxythiophene):poly(styrenesulfonate)

(PEDOT:PSS)/perovskite/phenyl- $C_{60}$ -butyric acid methyl ester (PCBM)/cathode, in which PEDOT:PSS and PCBM play the roles of the hole transporting layer (HTL) and ETL, respectively. Although inverted PHJ PVSCs based on PEDOT:PSS HTL have achieved impressive PCEs,<sup>14</sup> there are still challenges for PEDOT:PSS to serve as the HTL.<sup>13,15,16</sup> For instance, perovskite

<sup>&</sup>lt;sup>a</sup> Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou, 510640, China. E-mail: msbzhang@scut.edu.cn;

msangusyip@scut.edu.cn.

<sup>&</sup>lt;sup>b.</sup> Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen, 518060, China. E-mail: songjun@szu.edu.cn.

<sup>&</sup>lt;sup>+</sup> G. Chen and F. Zhang contributed equally

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films grown directly on PEDOT:PSS exhibit incomplete surface coverage and apparent pinholes, which result in poor device performance.<sup>15,16</sup> To solve this problem, Huang et al. introduced non-wetting poly(bis(4-phenyl)(2,4,6а trimethylphenyl)amine) (PTAA) layer as the HTL, and obtained perovskite grains with a high average aspect  $\operatorname{ratio.}^{17}$  As a result, these PVSCs exhibited excellent performance with a PCE as high as 18.1% due to the reduced perovskite grain boundary area and increased crystallinity. In addition to improving the perovskite morphology, the shallower lowest unoccupied molecular orbital energy level (ELUMO) and deeper highest occupied molecular orbital energy level ( $E_{HOMO}$ ) of PTAA enables it to efficiently block electrons and increase the builtin potential  $(V_{bi})$  within the device, respectively.<sup>18</sup> Regarding the choice of ETM, PCBM has been proven as one of the most effective ETMs for inverted PHJ PVSCs due to its relatively high electron mobility, suitable energy level, and roomtemperature and orthogonal solvent processability.<sup>19,20</sup> While other ETMs, such as n-type conjugated polymers<sup>21,22</sup> and discotic molecules,<sup>23</sup> have also been explored as efficient cathode interfacial layers for p-i-n PHJ PVSCs.

Several strategies have been developed to improve the performance of inverted PHJ PVSCs, such as the introduction of advanced methods for fabricating perovskite films,<sup>24-26</sup> compositional engineering of perovskite  $\mathsf{films}^{27,28}$  and interfacial engineering.<sup>29–32</sup> The latter method is of particular interest to material chemists as new materials with tailored interfacial properties can be rationally designed to improve the interfaces and device performance of PVSCs. At the perovskite/PCBM/cathode side, although low work-function (WF) metal cathodes, such as Ca (WF of ~2.9 eV), can achieve large  $V_{bi}$  values that are favorable for exciton dissociation, as well as charge transport and extraction,<sup>33</sup> their extremely high reactivity to oxygen and moisture in air often leads to insufficient device stability. On the contrary, relatively stable metals, such as AI (WF of ~4.3 eV), Ag (WF of ~4.7 eV) and Au (WF of ~5.2 eV), are more desirable for realizing long-term stable devices.<sup>34–36</sup> However, the relatively large mismatch between the WFs of these metals and the  $E_{LUMO}$  of PCBM produces small  $V_{bi}$  values and inferior device performance.<sup>37</sup> Moreover, as PCBM shows limited conductivity, only relatively thin films of it can be used, which therefore may lead to incomplete coverage on the rough perovskite film. In such a situation, direct contact of the metal atoms (e.g., Al or Ag) with the perovskite film could happen, resulting in poor device performance and stability.<sup>38</sup> A versatile approach to address these issues is to insert a cathode interfacial layer (CIL) to further modify and improve the interface between the PCBM and metal cathode. For instance, Snaith et al. developed goodperformance and flexible PVSCs containing a low temperature processed n-type TiO<sub>x</sub> layer between the PCBM/Al interface.<sup>35</sup> The TiO<sub>x</sub> CIL could serve as a hole-blocking layer and also prevent metal diffusion into the PCBM, thus improving the PVSC performance. Yuan and coworkers also demonstrated that a solution processed bathocuproine (BCP) CIL<sup>40</sup> could reduce leakage current and improve the fill factor (FF) of PVSCs since BCP can planarize the perovskite/PCBM surface for better contact with the metal cathode and improve the charge transfer rate at the cathode interface.

In addition to inorganic CILs, amine-functionalized polymers and small molecules, which have been demonstrated to be an effective class of CILs for organic photovoltaics (OPVs),<sup>41-43</sup> were also successfully used to adjust the interfacial properties of PCBM/cathode in PVSCs.<sup>38,44–47</sup> Since these CILs can be processed at low temperature from alcohols, low-cost and solution-processed multilayer PVSCs can be realized without interfacial mixing or erosion, which is highly critical for highperformance devices. For example, Xue et al. employed an alcohol-soluble and amino-functionalized polymer, PN<sub>4</sub>N, to improve the PCBM/AI interface, and the PCE was enhanced from 12.4% (without any CIL) to 15.0% (with  $\text{PN}_{4}\text{N}$  CIL).  $^{46}$ Zhang et al. demonstrated that the PCE of a PVSC device based ITO/PEDOT:PSS/MAPbI<sub>3-x</sub>Cl<sub>x</sub>/PCBM/CIL/Ag on could be improved from 10.0% (without any CIL) to 14.0% by incorporating a methanol-processed perylenediimide CIL.38 One of the probable working mechanisms for these CILs is that the ionic or polar groups within the CILs can interact with high-WF cathodes, leading to the generation of oriented interfacial dipoles that can reduce the WFs of the cathodes.<sup>48</sup> The decreased WFs of cathodes can increase the  $V_{his}$  across PVSC devices, which is beneficial for charge transport and extraction, enhancing R<sub>sh</sub>s and finally boosting the open circuit voltage  $(V_{ac})$  and FF. A second mechanism may be that the lone-pair electrons or anions within CILs can n-dope the PCBM, which increases the electron mobility of PCBM layers, diminishes the device  $R_s$  values and improves the circuit current density  $(J_{sc})$  and FF.<sup>49</sup> The other function of CILs possibly lies in improving the hydrophilicity of PCBM and thus its compatibility with metal cathodes.<sup>42</sup> Therefore, in order to achieve high-performance inverted PHJ PVSCs fabricated by low-temperature solution processing technologies, it is important to modify the cathode interfaces by introducing surfactant-like CILs.

One of the existing problems of reported CILs is that their  $E_{LUMO}$  values are typically higher than those of fullerene ETLs. Mismatches in  $E_{LUMO}$  may affect the charge transfer properties between the ETL/CIL interfaces. Ideally, a CIL with a deep  $E_{LUMO}$  (~-4.0 eV) that matches well with that of the fullerene ETL will be beneficial for improving the electron transport from the ETL to the metal cathode. Alternatively, pyridinium salts, which show deep  $E_{LUMO}$  and have been proven to be efficient CILs for OPVs, <sup>48,50</sup> may be even more efficient CILs for PVSCs.

Herein, we present high-performance inverted PHJ PVSCs, based on an ITO/PEDOT:PSS/PTAA/MAPbl<sub>3</sub>/PCBM/CIL/Al system, by introducing a newly developed bispyridinium salt (**FPyBr**) as the CIL. The deep-lying  $E_{LUMO}$  of **FPyBr** offers good energy level alignment with both PCBM and Al, and its high ionization potential can effectively block the undesired hole carriers from reaching the cathode. In addition, **FPyBr** can efficiently n-dope PCBM by the Br<sup>-</sup> anion, which not only increases the electron mobility of PCBM, but also creates more efficient conductive pathways for electron transport. As a result, an almost hysteresis-free PCE of 19.61% is obtained under 100 mW cm<sup>-2</sup> illumination, compared to the bare-Al

device with a PCE of 16.97%, suggesting that **FPyBr** is a promising CIL for improving the performance of PVSCs.

#### **Results and discussion**

#### Synthesis and characterization

The synthetic route for the bispyridinium salt FPyBr is outlined in Scheme 1. 5-Bromo-[2,2']bipyridinyl (1) was prepared by 5-bromo-2-iodopyridine with reacting tributylstannanylpyridine under the conditions of a palladiumcatalyzed Stille cross-coupling reaction. The palladiumcatalyzed Suzuki cross-coupling reaction between 2,7bis(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-9,9-dioctylfluorene and 1 gave 2,7-bis-([2,2']bipyridinyl-5-yl)-9,9-dioctylfluorene (FPy) as a colorless oil. Then, the bispyridinium salt FPyBr was obtained by intermolecular cyclization between FPy and 1,2-dibromoethane in 125 °C. The chemical structures of compound 1, FPy (see the Supporting Information, Figure S1) and **FPyBr** (Figure S2) were verified by <sup>1</sup>H NMR, <sup>13</sup>C NMR and elemental analysis. FPy is readily soluble in low-polarity organic solvents (e.g., toluene, CHCl<sub>3</sub> and tetrahydrofuran [THF]) and cannot be dissolved in highly polar solvents (e.g., dimethyl sulfoxide [DMSO], methanol and ethanol). However, after quaternization, FPyBr shows excellent solubility in highpolarity solvents, including DMSO, methanol, ethanol and dimethyl formamide (DMF), but is insoluble in solvents with lower polarity (e.g., toluene, CHCl<sub>3</sub> and THF). This unique characteristic offers orthogonal solution dissolution processability for depositing FPyBr on non-polar PCBM films without eroding the layers underneath, thereby forming a robust CIL for inverted PHJ PVSCs.

#### **Thermal properties**

The thermal properties of **FPyBr** were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), as shown in Figure 1. From the TGA study, **FPyBr** shows a 5% weight loss temperature ( $T_d$ ) of 295 °C, confirming its high thermal stability. The DSC curve reveals the well-defined glass transition temperature ( $T_g$ ) of 134 °C, which suggests that **FPyBr** is amorphous in nature.

#### **Optical properties**

The UV-Vis absorption and photoluminescence (PL) spectra of **FPyBr** in methanol and film were measured, as shown in Figure 2, and the optical parameters are summarized in Table 1. **FPyBr** exhibits dominant absorption peak at 431 nm in methanol, which is assigned to the  $\pi$ - $\pi$ \* transition of the conjugated backbone. Compared with the absorption

spectrum in solution, a slightly spectral red shift is observed in the film as a result of weak intermolecular aggregation in the solid state. In the molecular structure of **FPyBr**, probably it exists torsion angle between two adjacent pyridinium rings due to the exclusion effect between the two N<sup>+</sup> ions, which reduces the planar conformation of conjugated backbone. The decreased planar conformation as well as the short conjugation could induce weaker intermolecular aggregation in solid state. The optical band gap ( $E_g^{opt}$ ) estimated from the band edge of the absorption spectrum in the film is 2.46 eV. In addition, the PL spectra display similar profiles both in solution and film form, with the same peaks at 553 nm.

#### **Electrochemical properties**

Cyclic voltammetry (CV) was employed to investigate the electrochemical properties of FPyBr, as shown in Figure 3. The oxidation potential of ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) was measured to be 0.42 eV relative to the reference electrode (saturated calomel electrode, SCE), and the redox potential  $(E_{red})$  of **FPyBr** was tested to be -0.30 eV under the same experimental conditions. The  $E_{LUMO}$  was calculated to be -4.08 eV according to the equation of  $E_{LUMO} = -e(E_{red} + 4.80 - 0.42)$ (eV), which means a good energy level alignment with both PCBM and Al, and thereby is beneficial for electron extraction at the cathode side. The  $E_{HOMO}$  was estimated to be -6.54 eV according to the equation of  $E_{HOMO} = E_{LUMO} - E_g^{opt}$ . This deeplying  $E_{HOMO}$  is in favor of blocking hole carriers from the perovskite layer into the cathode, which can reduce leakage current and charge recombination loss at the cathode interface.

#### Photovoltaic performance of perovskite solar cells

To investigate the cathode modification ability of FPyBr, we fabricated inverted PHJ PVSCs with the structure of ITO/PEDOT:PSS/PTAA/MAPbl<sub>3</sub>/PCBM/FPyBr/Al (Figure 4a). The PTAA layer was used to improve the interface between PEDOT:PSS and MAPbl<sub>3</sub> layers, providing better E<sub>HOMO</sub> matching and an electron blocking effect for more efficient hole extraction at the anode.<sup>17,18</sup> For comparison, reference PVSCs without the FPyBr CIL were also fabricated. The detailed procedures for preparing the MAPbl<sub>3</sub> film and other functional layers (except FPyBr layer) can be found in a previous report.<sup>51</sup> The X-ray diffraction (XRD) pattern of MAPbI<sub>3</sub> agrees well with the crystalline structures of MAPbl<sub>3</sub> in previous reports (Figure S3a).<sup>52,53</sup> The CILs with a thickness of about 4 nm were deposited on PCBM layers by spin coating a FPyBr solution (0.3 mg mL<sup>-1</sup> in ethanol) at 6000 rpm for 20 s. A schematic of the energy level of each layer is shown in Figure 4b.



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Scheme 1. Synthetic route for FPyBr.



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Figure 2. a) UV-vis absorption and b) PL spectra of FPyBr.



The top-view scanning electron microscopy (SEM) image of the MAPbl<sub>3</sub> film shows a uniform and compact morphology with a large crystal grain size (Figure 4c). The cross-sectional SEM image of the PVSC device without a cathode displays a well-defined layered structure with sharp interfaces (Figure 4d). It can be observed that the MAPbI<sub>3</sub> grain size in the vertical direction is comparable to the perovskite film thickness, which is the ideal condition for carrier transport and collection, since the chance of charge carriers being quenched at grain boundaries can be minimized.<sup>51</sup> Although the ultrathin FPyBr layer is not entirely obvious in the cross-sectional SEM image, an X-ray photoelectron spectroscopy (XPS) measurement on the ITO/PCBM/FPyBr surface confirms its existence on PCBM, since the N 1s (398.2 and 398.6 eV) and Br 3d (63.8 eV) peaks can all be detected (Figure S3b).

Current density versus voltage (J-V) characteristics of the inverted PHJ PVSCs with or without FPyBr CIL are shown in Figure 5a, and their photovoltaic performance parameters are listed in Table 2. The reference device without the FPyBr layer exhibits a PCE of 16.97%, with a  $V_{oc}$  of 1.11 V,  $J_{sc}$  of 22.50 mA  $\mbox{cm}^{-2}$  and FF of 67.8% under reverse scanning conditions. Interestingly, after introducing the FPyBr layer, the PCE increases to 19.61%, with a  $V_{oc}$  of 1.11 V,  $J_{sc}$  of 23.19 mA cm<sup>-2</sup> and FF of 76.0% under reverse scanning conditions. As a comparison, we also studied the FPyBr layer effect on photovoltaic performance by varying the concentration of FPyBr in ethanol, and the related J-V curves and photovoltaic parameters are presented in Figure S4 and Table S1, respectively. It can be found that the best processing concentration for **FPyBr** is 0.3 mg mL<sup>-1</sup>. The external quantum efficiency (EQE) of the FPyBr-based device shows values higher than 80% over the whole visible region, and the maximum value reaches over 90% (Figure 5b). The calculated  $J_{sc}$  from integrating the EQE spectrum is 22.77 mA cm<sup>-2</sup>, with a difference of about 2% relative to the measured  $J_{sc}$ , suggesting

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an accurate measurement in this study. Alternatively, the **FPyBr**-based PVSC displays a PCE as high as 19.32% (with  $V_{oc}$  = 1.11 V,  $J_{sc}$  = 23.11 mA cm<sup>-2</sup> and FF = 75.4%) under forward scanning conditions (Figure 5c and Table 2). The PCE difference between various scanning directions is smaller than 1.5%, indicating a low hysteresis effect, which is important for achieving high-performance and stable PVSCs. In order to evaluate the stability of the power output of the **FPyBr**-based PVSCs, the steady-state photocurrent and efficiency were

measured by applying a constant bias voltage at the maximum power point. As shown in Figure 5d, we obtain a steady-state PCE of 19.4% for the **FPyBr**-based device at a constant bias voltage of 0.92 V, which is in good agreement with the average PCE of the *J*-V curves with both reverse and forward scanning directions. To check the reproducibility of the **FPyBr**-based devices, a histogram of PCE values obtained from 43 devices is summarized in Figure S5, which implies that most of the PVSCs can achieve high photovoltaic performance.



Figure 4. a) Configuration of the inverted PHJ PVSC. b) Schematic of the energy level of each layer. c) Top-view SEM image of MAPbI<sub>3</sub> film on the surface of ITO/PEDOT:PSS/ PTAA films. d) Cross-sectional SEM image of the PVSC device without cathode.



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Figure 5. Photovoltaic performance characteristics under AM 1.5G solar irradiation. a) *J-V* curves of the PVSCs with or without the FPyBr CIL. b) EQE spectrum and integrated photocurrent curve of the FPyBr-based PVSC. c) *J-V* curves of the FPyBr-based PVSC with different scanning directions. d) Steady-state PCE and photocurrent of the FPyBr-based PVSC measured at the maximum power point.

Table 2. Photovoltaic performance parameters of the PVSCs with or without FPyBr CIL under AM 1.5G irradiation.

CIL	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE <sub>max</sub> (%)	PCE <sub>avg</sub> (%)	R <sub>s</sub> (Ω cm <sup>2</sup> )	R <sub>sh</sub> (Ω cm <sup>2</sup> )
w/o <b>FPyBr</b> (reverse)	1.11	22.50	67.8	16.97	16.35	7.6	990.1
FPyBr (reverse)	1.11	23.19	76.0	19.61	18.93	5.7	2809.9
FPyBr (forward)	1.11	23.11	75.4	19.32	18.72	5.3	1339.9

The improvement of PVSC performance after inserting the FPyBr CIL is attributed to the significantly increased FF and slightly enhanced J<sub>sc</sub>. Compared to the bare-Al device, the introduction of FPyBr with a suitable ELUMO can induce better energy alignment and ohmic contact between PCBM and Al, which facilitate electron transport and extraction, and decrease interfacial recombination at the cathode side, leading to a higher J<sub>sc</sub> and FF, which have been reported in the case of OPVs.<sup>54,55</sup> Moreover, **FPyBr** with its deep-lying  $E_{HOMO}$  can serve as an efficient hole-blocking layer to improve the charge selectivity, which reduces leakage current, as well as electronhole recombination loss at the cathode interface, and finally improves the FF and  $J_{sc}$ .<sup>30</sup> The obviously increased  $R_{sh}$  from 990.1  $\Omega~\text{cm}^2$  for the bare-Al device to 2809.9  $\Omega~\text{cm}^2$  for the FPyBr-based device confirms that the leakage current and/or charge recombination can be reduced after introducing the FPyBr CIL.<sup>46</sup>

It is well known that for both PVSCs and OPVs, the introduction of alcohol-soluble ionic polymers<sup>56</sup> or small molecules<sup>44</sup> can often decrease the WFs of cathodes and also introduce interfacial n-doping to PCBM, facilitating better electron transport from the active layers to cathodes. In our case, the  $V_{oc}$  values of the bare-Al and **FPyBr**-based devices show the same value, which suggests that the WF matching effect may only play a minor role in improving device performance. Therefore, we further investigate the n-doping effect induced by the FPyBr CIL to PCBM. Amine- or ammonium salt-functionalized CILs are known to n-dope PCBM via the lone-pair electrons or anion-induced electron transfer process, which induce more efficient conductive pathways to improve electron transport and extraction. 54,57,58 We electron paramagnetic resonance (EPR) performed spectroscopy to study the electron transfer phenomenon in our PVSCs (Figure 6a). The sole component of PCBM or FPyBr shows no detectable EPR signal, while the blend of PCBM and **FPyBr** (1:1, w/w) displays intense anionic fullerence absorption, which suggests electron transfer from Br<sup>-</sup> to PCBM occurred.

The influence of the **FPyBr** layer on the charge transport properties of the PCBM layer was studied through the electron-only devices with the structures of AI/PCBM/AI and

Al/PCBM/**FPyBr**/Al, and the electron mobilities were extracted by fitting the data with the space charge limited current (SCLC) model (Figures 6b and S6).<sup>59</sup> The deposition conditions of PCBM and **FPyBr** were the same as those used for the PVSC fabrication. In comparison with the Al/PCBM/Al device with an electron mobility of  $4.0 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, the Al/PCBM/**FPyBr**/Al device exhibits a much higher electron mobility of  $1.1 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. The enhanced electron mobility probably results from the removal of the PCBM surface traps via n-doping by **FPyBr**, which decreases the transient time of the electrons through the film.<sup>54</sup> Note that the increase in electron mobility is also consistent with the result of reduction in  $R_s$  of the PVSC after inserting the **FPyBr** layer, which leads to a higher FF and  $J_{sc}$ .

Steady-state PL and time-resolved PL (TRPL) decay measurements were performed to study the charge transfer properties at the MAPbl<sub>3</sub>/PCBM interfaces (Figures 7 and S7). All the samples (MAPbl<sub>3</sub>, MAPbl<sub>3</sub>/PCBM and MAPbl<sub>3</sub>/PCBM/FPyBr) exhibit steady-state PL peaks at 775 nm originating from MAPbI<sub>3</sub>. The PL intensity of the perovskite layer coated with PCBM is obviously lower than that of the pristine perovskite layer. Note that depositing the FPyBr layer on the PCBM surface induces more significant PL quenching, which implies that FPyBr can increase the degree of charge transfer at the MAPbl<sub>3</sub>/PCBM interface.<sup>27</sup> From the TRPL curves, the MAPbl<sub>3</sub>/PCBM/FPyBr sample displays a shorter fluorescence lifetime than the MAPbl<sub>3</sub>/PCBM film sample, which means that the electron-hole separation at the MAPbl<sub>3</sub>/PCBM interface is more efficient after introducing a **FPyBr** layer.<sup>60</sup> The improvement in charge transfer properties by FPyBr is probably due to the increased electron mobility of the PCBM layer by FPyBr, which decreases the trap-assisted recombination of electrons and holes at the MAPbl<sub>3</sub>/PCBM interface.<sup>61</sup> The slightly deeper  $E_{LUMO}$  of **FPyBr** than that of PCBM may also make electron injection from MAPbI<sub>3</sub> into PCBM easier.

We used atomic force microscopy (AFM) to study the influence of the FPyBr layer on the morphology of the ITO/PCBM films (Figure 8a-c). The pristine and ethanol-treated PCBM films both show smooth surfaces with root mean square (rms) roughnesses of 1.13 and 1.00 nm, respectively. Dramatically, after depositing the FPyBr layer on top of PCBM, the surface becomes smoother with a rms roughness of 0.711 nm, probably because FPyBr molecules fill the voids in the PCBM surface. The improved surface smoothness and uniformity of the PCBM/FPyBr bilayer may form better contact with the AI cathode, thus reducing leakage current at the cathode.<sup>62</sup> Moreover, FPyBr may also serve as a protective layer to reduce the diffusion of Al atoms into the MAPbI<sub>3</sub>/PCBM layers, owning to the strong metal coordination property of the bispyridinium unit in FPyBr. In addition, measurements of the static water contact angle ( $\theta$ ) were performed to study the wetting properties of the ITO/PCBM

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films with different treatments (Figure 8d-f). The pristine PCBM film displays an intensely hydrophobic surface with a  $\theta$  of 105.3°, which is not beneficial for contact with the metal cathode. After spin-coating ethanol on top, the PCBM surface shows a slight change in wetting ( $\theta$ = 103.2°). Interestingly, the deposition of **FPyBr** atop the PCBM film enhances the

hydrophilicity significantly, with a  $\theta$  value of 79.8°. The improved hydrophilicity contributes to better wettability and compatibility with the top metal cathode, which is favorable for decreasing the contact resistance at the cathode interface, thus increasing the FF.<sup>63</sup>



Figure 6. a) EPR spectra of different components in the solid state. b) J<sup>1/2</sup>-V characteristics of the electron-only devices with or without the FPyBr CIL (device structure: AI/PCBM/CIL/AI).



Figure 7. a) Steady-state PL and b) fitted TRPL decay measurements of different samples. The films were deposited on ITO/PEDOT:PSS/PTAA surfaces and the deposition conditions of all layers were the same as those for the PVSC fabrication.

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Figure 8. AFM images of different films: a) ITO/PCBM, b) ITO/PCBM/ethanol, and c) ITO/PCBM/FPyBr; static water contact angle images of different films: d) ITO/PCBM, e) ITO/PCBM/ethanol, and f) ITO/PCBM/FPyBr. The deposition conditions of all the films were the same as those for the PVSC fabrications.

#### Conclusions

In summary, we demonstrate high-performance and lowhysteresis inverted PHJ PVSCs by inserting a FPyBr layer between PCBM and Al. Compared to the bare-Al device with a PCE of 16.97%, the PVSC with the FPyBr CIL achieves simultaneous enhancements in FF and  $J_{sc}$ , and thus a boosted PCE as high as 19.61%. The improvements in FF and  $J_{sc}$  mainly result from the following contributions: (1) the suitable  $E_{LUMO}$ of FPyBr offers good energy level alignment with both PCBM and Al, and the high ionization potential can block holes from transporting into the cathode; (2) the n-doping to PCBM by Br within FPyBr induces efficient conductive pathways for electron transport; (3) the increased electron mobility of the PCBM layer by FPyBr modification leads to more efficient charge transfer and transport; (4) the smooth and uniform FPyBr layer serves as a protector to prevent Al atoms from contacting with PCBM and the perovskite, thus decreasing the leakage current; (5) the increased hydrophilicity of the PCBM film by FPyBr improves the wettability and compatibility with the metal cathode, and consequently lowers the contact resistance. Therefore, we conclude that this kind of novel bispyridinium salt is a promising cathode modifier for highperformance and low-hysteresis organic-inorganic hybrid lead halide perovskite solar cells. Our demonstration can also provide important guidelines for designing new generation interfacial materials for highly efficient perovskite solar cells.

#### **Experimental section**

#### Materials

All reagents, unless otherwise specified, were obtained from Aladdin Chemical Co. (Shanghai, China), Sigma Aldrich Chemical Co. (St. Louis, MO, USA), Alfa Aesar Chemical Co. (Ward Hill, MA, USA) or J&K Chemical Co. (Beijing, China), and were used as received. Clevios PVP AI 4083 PEDOT:PSS was bought from Heraeus (Hanau, Germany). PCBM was purchased from Nichem Fine Technology Co. Ltd. (Hsinchu County, Taiwan). The solvents were further purified by general procedures and were distilled before used. All air and water sensitive synthetic manipulations were performed under a dry argon atmosphere. 2,7-Bis(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-9,9-dioctyl-fluorene was synthesized according to a published paper.<sup>64</sup>

#### General measurements and characterization

<sup>1</sup>H NMR and <sup>13</sup>C NMR measurements were carried out on a Bruker AV-500 spectrometer (Bruker, Rheinstetten, Germany) operating at 500 MHz (for <sup>1</sup>H) and 75 MHz (for <sup>13</sup>C) with tetramethylsilane as the internal reference. APCI-MS analyses were obtained from an Acquity Waters UPLC equipped with a Waters Acquity TQ detector (Thermo Finnigan LCQ Fleet system; Waters, Milford, MA, USA). Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co., Langenselbold, Germany). TGA was conducted using a NETZSCH TG 209 at a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> flow. DSC was measured on a Netzsch DSC 204 under N<sub>2</sub> flow at a heating rate of 10 °C min<sup>-1</sup> and a cooling rate of 20 °C min<sup>-1</sup>. UV-vis absorption spectra were performed on a HP 8453 spectrophotometer. PL spectra were recorded on an Instaspec IV CCD spectrophotometer (Oriel Co., Stradford, CT, USA). CV was characterized on a CHI600D electrochemical workstation with a standard three electrode cell based on a Pt wire counter electrode and a platinum (Pt) working electrode, against a saturated calomel electrode as the reference electrode at a scan rate of 50 mV  $s^{-1}$  within a nitrogen-saturated anhydrous  $L^{-1}$ solution of 0.1 mol tetrabutylammonium hexafluorophosphates (Bu<sub>4</sub>NPF<sub>6</sub>) in acetonitrile, versus ferrocene/ferrocenium ( $Fc/Fc^{+}$ ) as the internal reference. Scanning Kelvin probe microscopy tests were implemented on a KP Technology SKP5050.

#### Synthesis

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5-Bromo-[2,2']bipyridinyl (1). Into a 50 mL of three-neck flask were added 5-bromo-2-iodopyridine (2.0 g, 7.0 mmol), 2tributylstannanylpyridine (2.6 g, 7.0 mmol), 20 mL of anhydrous toluene and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.58 g, 0.50 mmol) under argon flow. The reaction was heated to 120 °C and stirred overnight with argon protection. The mixture was cooled to room temperature and evaporated. The crude product was purified by column chromatography to afford compound 1 as a white solid (1.3 g, 79%).  ${}^{1}$ H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.71 (s, 1H), 8.66-8.65 (d, J = 5 Hz, 1H), 8.37-8.36 (d, J = 5 Hz, 1H), 8.32-8.31 (d, J = 5 Hz, 1H), 7.93-7.92 (d, J = 5 Hz, 1H), 7.82-7.80 (t, J = 5 Hz, 1H), 7.33-7.30 (m, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 154.67, 150.38, 150.30, 148.47, 139.70, 137.98, 124.24, 122.71, 121.58, 121.47. MS (APCI) m/z:  $[M + H]^+$  calcd for  $C_{10}H_7BrN_2$ , 235.1; found, 236.0. Anal. calcd for C<sub>10</sub>H<sub>7</sub>BrN<sub>2</sub>: C 51.09, H 3.00, N 11.92; found: C 51.28, H 3.19, N 11.71.

2,7-Bis([2,2']bipyridinyl-5-yl)-9,9-dioctyl-fluorene (FPy). 2,7-Bis(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-9,9-dioctylfluorene (0.57 g, 0.89 mmol), compound 1 (0.49 g, 2.1 mmol), 10 mL of toluene, K<sub>2</sub>CO<sub>3</sub> aqueous solution (2M, 2.7 mL) and  $Pd(PPh_3)_4$  (0.10 g, 0.087 mmol) were mixed in a 50 mL of three-neck flask under argon. The reaction was heated to 80 °C and stirred overnight under argon atmosphere. Then the mixture was cooled to room temperature and mixed with 20 mL of distilled water. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> for three times. The combined organic layer was washed with distilled water and brine before dried over anhydrous MgSO<sub>4</sub>. The organic solvent was distilled and the crude product was purified by column chromatography to afford FPy as a colorless oil (0.38 g, 61%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 9.02-9.01 (d, J = 5 Hz, 2H), 8.73-8.72 (d, J = 5 Hz, 2H), 8.53-8.52 (d, J = 5 Hz, 2H), 8.49-8.47 (d, J = 10 Hz, 2H), 8.12-8.10 (dd, J = 7.5 Hz, J = 2.5 Hz, 2H), 7.88-7.84 (m, 4H), 7.68-7.67 (dd, J = 5 Hz, J = 2.5 Hz, 2H), 7.65-7.64 (d, J = 5 Hz, 2H), 7.35-7.33 (m, 2H), 2.10-2.07 (m, 4H), 1.19-1.09 (m, 20H), 0.80-0.77 (m, 10H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ): 155.84, 154.64, 152.16, 149.21, 147.71, 140.70, 137.07, 136.92, 136.66, 135.22, 126.15, 123.74, 121.44, 121.14, 121.05, 120.60, 55.52, 40.33, 31.73, 29.97, 29.18, 29.17, 23.88, 22.58, 14.04. MS (APCI) m/z: [M +  $H_{49}^{\dagger}$  calcd for  $C_{49}H_{54}N_4$ , 699.0; found, 699.7. Anal. calcd for C49H54N4: C 84.20, H 7.79, N 8.02; found: C 84.03, H 7.88, N 8.09.

The bispyridinium salt (FPyBr). Compound FPy (0.20 g, 0.29 mmol) was dissolved in 15 mL of 1,2-dibromoethane under argon, and the solution was heated to 125 °C and stirred for 24 h. After being cooled to room temperature, the precipitate was collected by filtration. The solid was washed with tetrahydrofuran and acetone successively in a soxhlet extractor, and then dissolved in 5 mL of methanol and precipitated from 80 mL of ethyl acetate. The target compound was got by filtration to give a red solid (0.26 g, 82%). <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>,  $\delta$ ): 10.09 (s, 2H), 9.43-9.41 (dd, *J* = 7.5 Hz, *J* = 2.5 Hz, 2H), 9.40-9.38 (d, *J* = 10 Hz, 2H), 9.24-9.23 (d, *J* = 5 Hz, 4H), 8.99-8.96 (t, *J* = 7.5 Hz, 2H), 8.48-8.45 (t, *J* = 7.5 Hz, 2H), 8.41 (s, 2H), 8.31-8.29 (d, *J* = 10 Hz, 2H), 8.23-8.21 (dd, *J* = 10 Hz, *J* = 2.5 Hz, 2H), 5.46-5.45 (t, *J* = 2.5 Hz, 4H), 5.37-5.36 (t, *J* = 2.5 Hz, 4H), 2.29-2.26 (t, *J* = 7.5 Hz, 4H), 1.14-1.00

(m, 20H), 0.76-0.56 (m, 10H). <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>,  $\delta$ ): 153.08, 147.81, 147.64, 145.80, 143.55, 142.91, 141.20, 140.33, 138.06, 132.22, 130.27, 130.13, 128.16, 127.67, 122.77, 122.67, 56.30, 52.79, 52.65, 40.58, 31.52, 29.81, 29.16, 29.04, 24.10, 22.44, 14.36. Anal. calcd for C<sub>53</sub>H<sub>62</sub>Br<sub>4</sub>N<sub>4</sub>: C 59.23, H 5.81, N 5.21; found: C 59.09, H 5.97, N 5.10.

#### Solar cell fabrication and characterization

The MAI crystal was synthesized upon reaction of a concentrated aqueous solution of hydroiodic acid (HI) (15.0 mL, 57 wt.% in water, Aldrich) with methylamine (CH<sub>3</sub>NH<sub>2</sub>) (13.5 mL, 40 wt.% in aqueous solution, Aldrich) at 0 °C for 2 h with constant stirring under a nitrogen atmosphere. The precipitate was recovered by evaporation at 70 °C until completely dry. MAI was dissolved in ethanol at 90 °C, recrystallized from the supersaturated solution at room temperature, and then dried at 60 °C in a vacuum oven for 12 h. The perovskite precursor solution was prepared by mixing 922.0 mg of Pbl<sub>2</sub> (99.999%, Alfa Aesar) and 349.8 mg of MAI in 0.9 mL of DMF and 0.1 mL of DMSO, with a Pbl<sub>2</sub>: MAI molar ratio of 1:1.1.

The PEDOT:PSS solution was spun on top of the glass/ITO and annealed at 125 °C for 10 min. Then, the PTAA solution (2.5 mg mL<sup>-1</sup> in toluene) was spin-coated on the PEDOT:PSS layer at 6000 rpm and annealed at 100 °C for 5 min. The perovskite precursor solution (70 °C) was spin coated on the PTAA layer at 6000 rpm and, after 7 s of delay time, the wet film was washed with 200 µL of sec-butyl alcohol by uniformly dropping sec-butyl alcohol in the center of the substrate. After the spin stopped, the film was annealed on a hot plate at 100 °C for ~30 s. The film was then soaked with 200  $\mu L$  of secbutyl alcohol for 10 s, and subsequently dried by spin-coating at 6000 rpm for 30 s. The spin-coating processes were typically conducted in a glove box under a nitrogen atmosphere and with a real-time humidity of ~1 ppm. Finally, the film was subjected to a post-annealing treatment. In this step, the perovskite film was transferred onto a hot plate, first annealed in ambient air (real-time humidity of 55-65%) at 100 °C for 15 min, and then annealed in a DMSO atmosphere at 100 °C for 15 min. For the DMSO atmosphere, 50  $\mu$ L of DMSO solvent was dropped into a glass Petri dish, which was then used to cover the sample. Subsequently, PCBM (20 mg  $mL^{-1}$ , chlorobenzene) was spun on the perovskite layer at 2500 rpm. For the **FPyBr** sample, the **FPyBr** solution (0.3 mg mL<sup>-1</sup> in ethanol) was spin-coated on the PCBM layer at 6000 rpm for 20 s. Finally, the device was completed by evaporating a 100nm-thick aluminum film as the electrode (active area of 12 mm<sup>2</sup>).

SEM images and XRD patterns of the films were obtained with a Zeiss Supra 55 microscope and a Bruker QUANTAX 200 diffractometer, respectively. A sun simulator (Zolix Sirius-SS) was used to provide the simulated solar irradiation (AM 1.5G, 100 mW cm<sup>-2</sup>). *J-V* characteristics were measured using a Keithley 2400 source meter. The output of the light source was adjusted using a calibrated silicon photodiode (ABET technology). The *J-V* curves were measured by backward forward bias (1.2 V)  $\rightarrow$  negative bias (-0.5 V)—or forward—

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negative bias  $(-0.5 \text{ V}) \rightarrow$  forward bias (1.2 V)—scan. The EQE was measured using a power source (Zolix Sirius-SS) with a monochromator (Zolix Omni- $\lambda$ ) and a source meter (Keithley 2400). The steady-state PL spectra were measured by the fluorescence spectrophotometer (OmniPI-microS, Zolix, China), an excitation light of 325 nm came into the films from the air side. The time-resolved PL spectra were measured at 775 nm on the excitation at 600 nm by the time-correlated single photon counting (TCSPC) spectrometer (FLIM, Becker & Hickl GmbH, Germany). The device area (12 mm<sup>2</sup>) was determined by the overlap of cathode and anode. Notably, the presence of DMSO in the perovskite precursor solution probably alters the charge transport properties of the PEDOT:PSS layer. To avoid overestimation of the photocurrent, an aperture size of 12 mm<sup>2</sup> was used to define the light absorption area. All devices were measured immediately after fabrication without encapsulation in a super-clean lab with a controlled humidity of 55-65%

#### **Conflicts of interest**

There are no conflicts of interest to declare

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### **Graphical Abstract**

A novel bispyridinium salt (**FPyBr**) is designed as cathode modifier to achieve high-performance and low-hysteresis fullerene/perovskite solar cells with a maximal PCE of 19.61%. The suitable  $E_{LUMO}$  of **FPyBr** induces ideal ohmic contact at the cathode, and the deep  $E_{HOMO}$  provides efficient hole-blocking ability. **FPyBr** can increase the electron mobility of PCBM via n-doping, which improves charge transfer and transport.

