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Double fullerene cathode buffer layers afford highly efficient and stable inverted planar perovskite solar cells



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ABSTRACT

Fullerene derivatives especially [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) with strong electronaccepting abilities have been commonly implemented as indispensable cathode buffer layers (CBLs) of inverted (p-i-n) planar perovskite solar cells (iPSCs) to facilitate electron transport. However, only a single fullerene CBL is typically used in iPSC devices, resulting in interfacial energy offset between fullerene CBL and metal cathode and consequently insufficient electron transport. Herein, we synthesized a novel bis-dimethylaminofunctionalized fullerene derivative (abbreviated as PCBDMAM) and applied it as an auxiliary fullerene interlayer atop of PCBM to form a PCBM/PCBDMAM double fullerene CBL, leading to dramatic enhancement of both efficiency and ambient stability of iPSC devices. Incorporation of PCBDMAM interlayer facilitates the formation of interfacial dipole layer between PCBM and Ag cathode, resulting in decrease of the work function of the Ag cathode. As a result, the CH₃NH₃PbI₃ (MAPbI₃) iPSC devices based on PCBM/PCBDMAM double fullerene CBL exhibit the highest power conversion efficiency (PCE) of 18.11%, which is drastically higher than that of the control device based on single PCBM CBL (14.21%) and represents the highest value reported for double fullerene CBL-based iPSC devices. Moreover, due to the higher hydrophobicity of PCBDMAM than PCBM, iPSC devices based on PCBM/PCBDMAM double fullerene CBL shows an enhanced ambient stability, retaining 67% of the initial PCE after storage 1440 h exposure under the ambient atmosphere without any encapsulation, whereas only 43% retaining was achieved for the control device based on single PCBM CBL.

solar cells promises vast applications of PSCs.

commercialized crystalline-Si and inorganic semiconductor thin film

PSC device, inverted (p-i-n) planar PSCs (iPSCs) with the advantages of

the low-temperature solution processibility and negligible current-

voltage hysteresis have attracted more and more interests in recent

years [12-20]. To ensure efficient electron transport, a cathode buffer

layer (CBL) is typically required, which is incorporated between the

perovskite layer and cathode [21]. Fullerene derivatives especially [6, 6]-phenyl-C61-butyric acid methyl ester (PCBM) with strong

electron-accepting abilities have been commonly implemented as

indispensable CBLs of iPSC devices, fulfilling efficient electron transport

Among the popularly used planar heterojunction architectures of

1. Introduction

Organic-inorganic hybrid perovskite materials exemplified by $CH_3NH_3PbX_3$ (MAPbX₃, X = I, Br, Cl) have been drawing intense attentions in photoelectric conversion due to their tunable optical bandgaps [1–3], long electron-hole diffusion lengths [4], large absorption coefficients and excellent charge carrier transport properties [5–10]. During the past decade, extensive studies on perovskite solar cells (PSCs) employing organic-inorganic hybrid perovskite as light absorbers have been reported toward enhancement of device performance, enabling ever-increasing power conversion efficiency (PCE) reaching up to 25.2% [11]. Such a competitive PCE to those of the

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from the perovskite layer to cathode along with trap states passivation of perovskite surface [12,22,23]. However, only a single fullerene CBL is typically used for iPSCs, resulting in the existence of an interfacial energy offset between fullerene CBL and metal cathode since the Fermi level of the cathode such as Ag (-4.3 eV) is much lower than the lowest unoccupied molecular orbital (LUMO) of PCBM (-4.0 eV) [24-27]. This consequently leads to insufficient electron transport and inferior PCE. To promote electron transport from the perovskite layer to metal cathode for iPSC devices, substituting PCBM by other fullerene derivatives or incorporating an auxiliary interlayer between PCBM and cathode has been employed, and the latter strategy appears more feasible since no change in the fabrication procedure of the PCBM CBL is needed [19,28, 29]. So far most reported interlayer materials incorporated between PCBM and cathode are commercially available organic small molecules or polymers such as BCP, PEIE [24,30-37], which have nevertheless relatively low tolerance to moisture and/or oxygen and are thus detrimental to the ambient stability of iPSC devices. Alternatively, fullerene derivatives with high stability owing to the hydrophobic nature of the parent fullerene have been also applied as interlayers between PCBM and metal cathode, demonstrating enhanced efficiency via inhibiting interfacial charge recombination loss and improved device stability [38-42]. For instance, an amine functionalized fullerene derivative (DMAPA-C₆₀) composed of mixtures bearing different number of dimethylamino groups was applied by Azimi and Zhang et al. as an interlayer modifying PCBM CBL, leading to a dramatic increase of PCE from 9.4% to 13.4% for CH₃NH₃PbI_{3-x}Cl_x iPSC device, which is attributed to the formation of an interfacial dipole layer rendering optimum energy level alignment at the perovskite/PCBM interface [43]. Later on, Lei and Yang et al. applied another dimethylamino-modified fullerene derivative (PCBDAN) containing only one dimethylamino group as an alternative interlayer of CH₃NH₃PbI_{3-x}Cl_x iPSC devices, which exhibited an enhanced PCE of 17.2% due to decreased energy barrier between perovskite and Ag cathode accomplished by lowering the work function of Ag cathode [44]. Likewise, Russell et al. synthesized a fulleropyrrolidine derivative (C₆₀–N) bearing three dimethylamino groups and applied it as an interlayer modifying PCBM CBL of FA0.5MA0.5PbI3 iPSCs, achieving a high PCE of 15.5% which is much higher than that of the control device without interlayer (7.5%) due to the decreased work function of Ag cathode induced by C_{60} -N interfacial modification [25]. These studies reveal the importance of the amine group in not only making the hydrophobic fullerene derivative into alcohol-soluble material so as to realize orthogonal solvent processing of the interlayer but also facilitating the formation of dipole layer [36,45-49]. Noteworthy, most of these interlayer fullerene derivatives contain only one end amine group, limiting the interactions between fullerene derivatives with the atop metal cathode. Therefore, it is highly desirable to develop novel alcohol-soluble amine-functionalized fullerene derivatives bearing multiple amine groups as more efficient interlayers of iPSC devices.

Herein, we synthesized a novel PCBM-like bis-dimethylamino-functionalized fullerene derivative (abbreviated as PCBDMAM) via a facile esterification reaction. Upon applying PCBDMAM as an auxiliary fullerene interlayer atop of PCBM to form a PCBM/PCBDMAM double fullerene CBL, MAPbI₃ iPSC devices exhibit dramatic enhancements of both PCE and ambient stability relative to the control devices based on single PCBM CBL. The influence of PCBDMAM interlayer on the work function of Ag cathode deposited atop of PCBM was investigated, revealing that incorporation of PCBDMAM interlayer induced decrease of the work function of Ag cathode and facilitated the formation of interfacial dipole layer. Furthermore, involvement of PCBM/PCBDMAM double fullerene CBL was found to improve the ambient stability of the iPSC devices due to the higher hydrophobicity of PCBDMAM than PCBM.

2. Experimental section

2.1. Materials

Fluorine-doped tin oxide (FTO)-coated glass substrates were purchased from NSG Group, Japan, with a sheet resistance of $13 \pm 1.5 \Omega/sq$. PbI₂ was bought from Tokyo Chemical Industry Co., Ltd and MAI was purchased from Xi'an Polymer Light Technology Corp. Dimethylformamide (DMF, 99.8%), dimethylsulfoxide (DMSO, 99.8%) and chlorobenzene (99.9%) were obtained from Sigma-Aldrich. Isopropanol, ethanol, and acetone were all bought from Sinopharm Chemical Reagent Co., Ltd. C₆₀ was purchased from Suzhou Dade Carbon Nanotechnology Co. Ltd. PCBM (99.5%, Solenne Bv, Holand). Bathocuproine (BCP) was obtained from Alfa Aesar. All reactants and solvents were used as received without further purification.

2.2. Synthesis of bis (4-(2-(dimethylamino) ethoxy) phenyl) methanone (DMAM)

Synthesis of compound DMAM was referred to the method reported before [50]. The product is a white solid with the yield of 44.5%. ¹H NMR (400 MHz, CDCl₃, δ): 7.77 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 4.15 (t, *J* = 5.7 Hz, 2H), 2.78 (t, *J* = 5.7 Hz, 2H), 2.36 (s, 6H). ¹³C NMR (101 MHz, CDCl₃, δ): 194.45, 162.09, 132.19, 130.77, 114.01, 66.19, 58.14, 45.93.

2.3. Synthesis of bis (4-(2-(dimethylamino) ethoxy) phenyl) methanol (DMAM-OH)

Compound (DMAM) (400 mg, 1.12 mmol) was dissolved in 15 mL THF and then was cooled to 0 °C by ice bath. Later, LiAlH₄ (63.8 mg, 1.68 mmol) was added into the solution. Then, the reaction proceeded overnight with magnetic stirrer at room temperature under a nitrogen atmosphere. Finally, the reaction was quenched with water, and organic phase was extracted three times with dichloromethane. The organic solvent collected was dried over anhydrous MgSO₄. After removing the solvent, the product purified by silica gel column chromatography afford light yellow viscous liquid with the yield of 61.4%. ¹H NMR (400 MHz, CDCl₃, δ): 7.26 (d, *J* = 8.4 Hz, 4H), 6.85 (d, *J* = 8.7 Hz, 4H), 5.74 (s, 1H), 4.02 (t, *J* = 5.8 Hz, 4H), 3.47 (s, 1H), 2.71 (t, *J* = 5.8 Hz, 4H), 2.32 (s, 12H). ¹³C NMR (101 MHz, CDCl₃, δ): 157.96, 136.99, 127.71, 114.37, 75.08, 65.76, 58.15, 45.78.

2.4. Synthesis of PCBDMAM

To a solution of [6,6]-Phenyl-C₆₁-butyric acid (PCBA) (0.2 g, 0.22 mmol), compound DMAM-OH (0.2 g, 0.26 mmol), p-toluenesulfonic acid (p-TSA) (0.0424 g, 0.22 mmol), 4-dimethylaminopyridine (DMAP) (0.0272 g, 0.22 mmol), and diisopropylcarbinol (DIPC) (0.0197, 0.31 mmol) in 25 mL o-Dichlorobenzene were added. After that, the mixed solution was stirred by magnetic stirrer at room temperature under N2 atmosphere for 24 h. Then the solvent was removed under reduced pressure. The crude mixture was purified by silica gel column chromatography, affording a black solid product with the yield of 50.6%. ¹H NMR (400 MHz, CDCl₃, δ): 7.93–7.86 (m, 2H), 7.59–7.42 (m, 4H), 7.20 (d, J = 8.7 Hz, 4H), 6.86 (d, J = 8.8 Hz, 4H), 4.04 (t, J = 5.7 Hz, 4H),2.90–2.84 (m, 2H), 2.73 (t, J = 5.7 Hz, 4H), 2.59 (t, J = 7.4 Hz, 2H), 2.34 (s, 12H), 2.23–2.16 (m, 2H). ¹³C NMR (101 MHz, CDCl₃, δ): 172.08, 158.34, 148.77, 147.67, 145.77, 145.12, 145.07, 145.04, 144.97, 144.75, 144.72, 144.64, 144.61, 144.44, 144.31, 143.95, 143.70, 143.68, 142.98, 142.96, 142.92, 142.87, 142.19, 142.12, 142.08, 142.06, 140.91, 140.67, 138.01, 137.50, 136.66, 132.61, 132.08, 128.37, 114.44, 79.81, 65.79, 58.16, 51.85, 45.80, 34.35, 33.59, 22.35. MALDI-TOF m/z for PCBDMAM: [M]⁺ calcd for C₉₂H₄₀N₂O₄, 1236.31; found, 1236.82.



Scheme 1. Synthetic route and chemical structure of PCBDMAM. (i) Dimethylaminoethyl chloride hydrochloride, K₂CO₃, acetone. (ii) LiAlH₄, THF. iii) HCl, HOAc, toulene. (iv) DMAM-OH, p-toluenesulfonic acid (PTSA), diisopropylcarbinol (DIPC), 4-dimethylaminopyridine (DMAP), o-DCB, N₂.

2.5. Device fabrication

The FTO glass substrate was cleaned using detergent, deionized water, acetone, and isopropanol for 15 min and then dried under vacuum at 60 °C overnight. After the ultraviolet-ozone treatment for 15 min, the NiO_x precursor solution prepared by sol-gel process (0.1 mmol was dissolved in 10 mL ethanol and 60 µL ethanolamine, then stirred at 70 °C overnight) was spin-coated onto the FTO substrate in ambient atmosphere at 4000 rpm for 30 s and then dried at 280 $^\circ \mathrm{C}$ for 40 min. In the following step, the FTO substrate with NiOx film was transfer to a nitrogen-filled glovebox to fabricate MAPbI3 perovskite layer. Perovskite precursor solution composed of PbI2 (1.1 M), MAI (1 M) in DMF and DMSO (7:3 vol/vol) was dropped onto FTO/NiOx substrate by spincoating at 1000 rpm for 10 s and 4000 rpm for 45 s. After that, 80 µL chlorobenzene was drop-coated onto perovskite layer during the 25 s, the devices were annealed on a hot plate at 100 °C for 10 min. Later, PCBM (20 mg/mL in chlorobenzene) and PCBDMAM (0.03 mg/mL in isopropanol solution) were successively spin-coated onto MAPbI₃ perovskite film at 2000 rpm for 30 s and 1000 rpm for 30s, respectively, to form the ETL and CBL. Finally, Ag electrode (100 nm) was thermally evaporated onto the PCBDMAM layer under a pressure of about 10⁻⁵ Torr. Through the shadow mask, the active area of device was defined as 0.1 cm^2 .

2.6. Measurements and characterization

¹H NMR spectrum and ¹³C NMR spectrum was recorded on a Bruker AV 400 MHz NMR spectrometer and tetramethylsilane (TMS) was used as internal standard. MALDI-TOF Mass spectra were collected on a Bruker Autoflex Speed mass spectrometer. UV–vis spectra were recorded on UV–vis–NIR 3600 spectrometer (Shimadzu, Japan).

The current density-voltage (J-V) characterizations were detected by a Keithley 2400 source measurement unit under simulated AM 1.5 irradiation (100 mW cm⁻²) with a standard xenon-lamp-based solar simulator (Oriel Sol 3A). The simulator illumination intensity was calibrated with a mono-crystalline silicon reference cell (Oriel P/N 91150 V, with KG-5 visible color filter) calibrated by the National Renewable Energy Laboratory (NREL). Around 50 devices were prepared and detected independently to make sure that the results were reliable. The EQE measurements were carried out on an Oriel Intelligent Quantum Efficiency (IQE) 200TM measurement system with a tunable light source. SEM measurements were measured via a field-emission scanning electron microscope (Zeiss Gemini SEM 500, Germany). AFM measurements were obtained by using a XE-7 scanning probe microscope in noncontact mode (Park Systems, Korea). XPS measurements were performed on a Thermo ESCALAB 250 instrument with a monochromatized Al Ka X-ray source. The film thicknesses were measured by a KLA-

Tencor P6 surface profilometer. The steady-state photoluminescence (PL) spectra were determined through an Edinburgh Instruments FLS920 fluorescence spectrometer with an excitation wavelength of 460 nm. The time-resolved photoluminescence (TRPL) spectra were performed via the time-correlated single-photon counting method with a Picoquant Gmbh Solea Supercontinuum laser. Synchrotron radiation photoelectron spectra (HR-SRPES) measurements were carried out at the Catalysis and Surface Science Endstation at the BL11U beamline in the National Synchrotron Radiation Laboratory (NSRL), Hefei. The secondary electron cutoff spectra and valence band edge spectra were measured using synchrotron radiation light as the excitation source with photon energy of 40 eV. A sample bias of -5 V was applied to observe the secondary electron cutoff. Impedance spectroscopy measurements (EIS) were measured in the dark by using an electrochemical workstation (Autolab 320, Metrohm, Switzerland) in a frequency range of 1 Hz to 1 MHz under 1.0 V. Alternating current (AC) 20 mV perturbation was applied with a frequency from 1 MHz to 1 Hz. The obtained impedance spectra were fitted with ZView software (v2.8b, Scribner Associates). Water contact angles were obtained by using a CAM instrument (Data Physics, Germany).

3. Results and discussion

3.1. Synthesis and characterization of PCBDMAM

The novel bis-dimethylamino-functionalized fullerene derivative (PCBDMAM) was synthesized via a facile esterification reaction of [6, 6]-phenyl-C61-butyric acid (PCBA) with bis(4-(2-(dimethylamino) ethoxy) phenyl) methanol (DMAM-OH) as illustrated in Scheme 1. The detailed synthetic procedures are depicted in the experimental section (see Supporting Information S1). The solubility of PCBDMAM in chlorobenzene is ca. 20 mg/mL, smaller than that of PCBM, indicating that the involvement of bis-dimethyamino moieties deteriorates the solubility of PCBM due to increased molecular polarity. However, the existence of the bis-dimethylamino group makes PCBDMAM alcohol-soluble with a solubility of ca. 0.1 mg/mL in isopropanol. This enables the feasibility of orthogonal solvent processing of PCBDMAM layer atop of PCBM without destroying PCBM layer. Considering that synthesis mono-dimethylamino group fullerene derivative is difficult to exclude the effect of additional hydroxyl group, and it is reported that the more exposed amine groups, the more effective of WF's altering [45]. Therefore, we did not design and synthesize a single amine-functional fullerene derivative here for comparison.

The chemical structure of PCBDMAM was determined by ¹H and ¹³C NMR spectroscopies, FT-IR spectroscopy and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry. According to the ¹H NMR spectrum of PCBDMAM, proton signals of



Fig. 1. (a) The device structure of iPSCs based on fullerene derivative CBL and the chemical structures of PCBDMAM. (b) Top-view SEM image of MAPbI₃ perovskite film grown on NiO_x. (c) Cross-section SEM image of the iPSC device base on PCBDMAM CBL. (d) *J*-V curves of the control and PCBDMAM CBL-based device measured under illumination of AM 1.5G 100 mW/cm² in air. The scanning direction is from open-circuit voltage to short-circuit (reverse) voltage, and the scan speed is 100 mV/s (e) EQE spectra of the control and PCBDMAM CBL-based device measured in air.

phenyl, dimethylamino moieties are observed in the range of 6.85–7.91 ppm and at 2.34 ppm, respectively (see Supporting Information Fig. S5). In the ¹³C NMR spectrum, signals in the range of 132.1–148.8 ppm is assigned to the sp²-carbons of C₆₀ cage along with the phenyl ring moiety attached onto the bridgehead carbon (see Supporting Information Fig. S6). The other sp²-carbon signals at 114.4 and 128.4 ppm are assigned to the phenyl ring within the DMAM moiety. In addition, the ¹³C NMR signal at 172.1 ppm is assigned to carbonyl (–O–C=O) group. Furthermore, the sp³-carbon signals located at 45.8 ppm is assigned to the methyl group within the dimethylamino moiety.

MALDI-TOF mass spectrometry of PCBDMAM shows a dominant ionic peak at m/z = 1236, which is coincident with the molecular weight of PCBDMAM, confirming the proposed chemical structure (see Supporting Information Fig. S7). Furthermore, in the FT-IR spectrum of PCBDMAM, the C=C bending vibrations of the phenyl ring were observed at 1607, 1511, 1460 cm⁻¹, respectively. The characteristic vibrational peaks at 1738, 1240, and 1180 cm⁻¹ was assigned to the stretching vibrations of C=O, O–C and C–N bonds, respectively. Besides, the characteristic vibration peak of C₆₀ cage at 526 cm⁻¹ was clearly observed (see Supporting Information Fig. S8). The simultaneously existence of the characteristic vibrational peaks corresponding to C₆₀ cage and the addends confirm the chemical structure of PCBDMAM. The thermal stability of PCBDMAM was further evaluated by thermogravimetric analysis (TGA), revealing its excellent thermal stability with the decomposition temperature beyond 392.3 °C (5% weight loss, see Supporting Information Fig. S9).

3.2. Photovoltaic performance of iPSC devices based on PCBM/ PCBDMAM double fullerene CBL

In order to incorporate PCBDMAM layer without destroying the underneath PCBM layer, we spin-coated PCBDMAM dissolved in isopropanol with variable concentrations (0.01–0.1 mg/mL) onto PCBM layer at 1000 rpm. The optimized concentration of PCBDMAM in isopropanol was determined to be 0.03 mg/mL according to its performance in device efficiency enhancement (see Supporting Information Fig. S10). Given that the concentration of PCBDMAM in isopropanol is quite low, it is necessary to verify the existence of PCBDMAM film atop of PCBM layer. We carried out X-ray photoelectron spectroscopy (XPS) to probe the characteristic nitrogen signal of PCBDMAM. According to the comparison of the XPS survey and high-resolution N1s XPS spectroscopic results, the N1s signal at 399.6 eV is clearly observed for PCBM/PCBDMAM double fullerene CBL, which is however absent in the single PCBM film (see Supporting Information Fig. S11). This confirms

Table 1

Summary	of	photovoltaic j	parameters of	perovskite solar cells	with or withou	t PCBDMAM as C	BL obtained	under AM	A 1.5G s	simulated sun lig	ght.
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Device	CBL	Voc	V _{oc} J _{sc}		FF PCE (%)		$R_{\rm s}^{\rm b}$	$R_{\rm sh}^{\rm b}$
		(V)	(mA/cm ²)	(%)	Average ^a	Best	$(\Omega \cdot cm^2)$	$(\Omega \cdot cm^2)$
А	РСВМ	1.01 ± 0.02	20.31 ± 1.22	61.52 ± 2.47	12.58 ± 0.85	14.21	21.9	1566.8
В	PCBM/PCBDMAM	1.03 ± 0.01	21.51 ± 0.72	76.67 ± 1.57	17.12 ± 0.50	18.11	4.0	2164.8

^a Averaged over 50 devices fabricated independently.

^b R_s and R_{sh} are obtained by the PCE measurement system.



Fig. 2. (a) Ag 3d XPS spectra and b) synchrotron radiation photoelectron spectra (HR-SRPES) of the Ag electrode and PCBDMAM modified Ag electrode. (c) Schematic diagram of iPSCs with a CBL and the cathode interaction process. (d) The energy-level diagram of the iPSCs.

the existence of PCBDMAM film atop of PCBM layer.

Based on PCBM/PCBDMAM double fullerene CBL, we fabricated iPSC devices in glove box with the structure of FTO/NiOx/CH3NH3PbI3/ PCBM/PCBDMAM/Ag (Fig. 1a), in which a thin film of NiO_x (~20 nm) prepared by sol-gel process was used as hole transport layer (HTL) [51, 52]. A compact and dense perovskite film of \sim 300 nm without any pinhole was prepared by one-step method through spin-coating the precursor solution of PbI2:MAI (1.1:1, molar ratio) onto the surface of FTO/NiO_x film in nitrogen glovebox (Fig. 1b). For comparison, control devices based on the single PCBM CBL with and without isopropanol treatment were also fabricated. The current density-voltage (J-V) curves of the iPSC devices with and without PCBDMAM interlayer measured under one sun illumination are compared in Fig. 1d, and the corresponding photovoltaic parameters including open-circuit voltage (V_{oc}), short-circuit current (Jsc), fill factor (FF), PCE, series resistance (Rs), and shunt resistance (R_{sh}) are summarized in Table 1. The control device based on single PCBM CBL gives a V_{oc} of 1.01 V, a J_{sc} of 20.31 mA/cm², FF of 61.52%, and an average PCE of 12.58%. Upon incorporating PCBDMAM interlayer to form PCBM/PCBDMAM double fullerene CBL, the average PCE increases dramatically to 17.12% calculated from a V_{oc} of 1.03 V, a J_{sc} of 21.51 mA/cm², and a FF of 76.67%, and the best PCE reaches 18.11%, which is enhanced by \sim 27% relative to that of the control device based on single PCBM CBL (14.21%). To confirm the reliability of the iPSC device with PCBM/PCBDMAM double fullerene CBL, steady-state photocurrent output measurements at the maximum power point was performed. The iPSC device with PCBM/PCBDMAM double fullerene CBL exhibits sensitive light response with a stabilized PCE of 17.88% during the illumination period of 300 s, confirming the considerable reliability of the iPSC device with PCBM/PCBDMAM double fullerene CBL, which is much higher than that of the control device based on single PCBM CBL (see Supporting Information Fig. S12). No obvious hysteresis of J-V curves is observed for both devices (see Supporting Information Fig. S13 and Table S2). To rule out the influence of the isopropanol solvent, we fabricated control devices based on the single PCBM CBL treated with isopropanol by spin-coating isopropanol at 1000 rpm onto PCBM layer, and found that the average PCE decreases dramatically to 9.85% due primarily to the decrease of FF (see Supporting Information Fig. S10 and Table S1). This result confirms that the

dramatic PCE enhancement of device based on PCBM/PCBDMAM double fullerene CBL is indeed contributed by PCBDMAM interlayer. Noteworthy, the best PCE of 18.11% achieved in our present work represents the highest value reported for double fullerene CBL-based iPSC devices (see Supporting Information Table S3 and Fig. S14).

Interestingly, the PCE enhancement upon incorporation of PCBDMAM interlayer is primarily due to the increase of FF (from 61.52% to 76.67%, ~19.7% enhancement), whereas the increases of both J_{sc} (from 20.31 to 21.51 mA/cm², ~4.5% enhancement) and V_{oc} (from 1.01 to 1.03 V, ~1.9% enhancement) are much smaller. This is verified by analyzing the statistical photovoltaic parameters (PCE, FF, J_{sc} , and V_{oc}) based on 50 devices fabricated independently (see Supporting Information Fig. S15 for the box plots and Fig. S16 for the histograms of PCE). Besides, the slight increase of J_{sc} is consistent with the external quantum efficiency (EQE) measurement results, revealing that the EQE responses in the broad visible-light region of 400–750 nm for PCBM/PCBDMAM double fullerene CBL-based device are slightly higher than those for the control device based on single PCBM CBL (Fig. 1e).

To unveil the reasons responsible for the increase of FF upon incorporation of PCBDMAM interlayer, we carried out a series of morphological and spectroscopic characterizations. The influence of PCBDMAM interlayer on surface morphology of the underneath PCBM layer was investigated by atomic force microscopy (AFM). According to the comparison of the AFM height images of PCBM layers with and without PCBDMAM deposition, while the single PCBM film exhibits a smooth surface with the root mean square (RMS) roughness of 0.69 nm, deposition of PCBDMAM interlayer atop leads to a slight increase of the RMS roughness to 0.79 nm (see Supporting Information Fig. S17). Moreover, some irregular particles appear (see also Supporting Information Fig. S17 for the phase image), which were likely resulted from the aggregation of PCBDMAM molecules with amphipathic feature. However, these aggregates are too thin to affect the overall surface morphology of the MAPbI₃/PCBM film according to scanning electron microscopic (SEM) results (see Supporting Information Fig. S18). On the other hand, incorporation of PCBDMAM interlayer is found to impose negligible influence on the optical absorption of MAPbI3 as well (see Supporting Information Fig. S19).

It has been reported that the lone-pair electrons of nitrogen (N)



Fig. 3. (a) The steady-state PL spectra and (b) timeresolved PL (TRPL) spectra of MAPbI₃, MAPbI₃/ PCBM, MAPbI₃/PCBM/PCBDMAM films on glass substrate. (c) The dependence of V_{oc} on different light intensities for the devices with and without PCBDMAM CBL. (d) Nyquist plots (symbols) and fitting curves (solid lines) of the ac impedance spectra of the devices with and without PCBDMAM measured in dark under a reverse potential of 1.0 V. Inset is the equivalent circuit model employed for the fitting of the impedance spectra.

within the amine group can interact with Ag to form Ag–N bonds which are beneficial for electron extraction from PCBM to Ag cathode [53,54]. To monitor whether the dimethylamino groups of PCBDMAM interact with Ag either, we measured XPS spectra of ITO/Ag films with and without PCBDMAM deposition, and found that the Ag 3d_{5/2} and 3d_{3/2} signals of ITO/Ag film at 368.7 eV and 374.8 eV negatively shifted negatively to 368.3 eV and 374.3 eV respectively upon PCBDMAM deposition (Fig. 2a), suggesting the strong interaction between PCBDMAM and Ag electrode resulting in the formation of Ag–N bonds [53,54].

We further used synchrotron radiation photoelectron spectra (HR-SRPES) to monitor the influence of PCBDMAM on the work function of Ag electrode. According to the secondary electron cutoff of synchrotron radiation photoelectron spectra (HR-SRPES) (Fig. 2b) [55], the work functions of Ag electrodes before and after depositing PCBDMAM interlayer were calculated to be 4.38 eV and 3.75 eV, respectively (see Supporting Information S14), revealing the obvious decrease of the work function of Ag electrode after depositing PCBDMAM. This suggests that PCBDMAM interlayer can act as an interfacial dipole layer via the formation of Ag–N bonds as discussed above (Fig. 2c), inducing the decrease of the work function of Ag electrode decreased to 3.75 eV, consequently the interfacial energy offset between PCBM CBL and Ag cathode is minimized (Fig. 2d), facilitating electron transport from PCBM CBL to Ag [30,56].

In order to study the influence of PCBDMAM CBL on the electron transport process and interfacial charge recombination dynamics of iPSCs, steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) characterizations were performed [57]. As shown in Fig. 3a, a strong PL characteristic emission peak of the pristine perovskite film appears at 765 nm, which was quenched obviously after depositing PCBM single layer. The further quenching was observed upon depositing PCBDMAM interlayer onto PCBM layer, revealing the more efficient electron transfer from perovskite to PCBM/PCBDMAM double fullerene CBL. Additionally, we further performed the TRPL measurements to monitor the charge transfer kinetics change of perovskite layer after depositing PCBM single layer and PCBM/PCBDMAM double fullerene CBL with the architecture as glass/MAPbI₃/PCBM/PCBDMAM, glass/MAPbI₃/PCBM and glass/MAPbI₃ (Fig. 3b) and corresponding TRPL data fitted by the bi-exponential decay function were summarized (see supporting information S15). Relative to the control MAPbI₃ film with a lifetime of 34.11 ns, the perovskite film after depositing PCBM single layer exhibits a remarkable decreased lifetime of 4.89 ns and even smaller lifetime of 4.12 ns after depositing PCBM/PCBDMAM double fullerene CBL, suggesting the more effective charge transport from MAPbI₃ to PCBM/PCBDMAM double fullerene CBL [58,59]. In addition, we studied the relationships between V_{oc} and incident light intensity (P_{light}) to unveil the origin of PCE enhancement after depositing PCBDMAM interlayer atop PCBM layer (Fig. 3c) by plotting V_{oc} as a function of incident light intensity according to the following formula:

$$V_{oc} \propto \frac{nkT}{q} \ln(P_{light}) \tag{1}$$

where k is Boltzmann constant, T is absolute temperature, q is electron charge, and n is the ideal factor related to the dominant charge recombination mechanism [60,61]. Slope larger than kT/q demonstrates that monomolecular recombination was occurred at the interface, indicating the existence of trap states. The n value corresponding to monomolecular recombination process shown that the iPSC device based on PCBM/PCBDMAM double fullerene CBL have lower value of 1.03 than that of the control device with PCBM single CBL (n = 1.22), implying the enhanced trap state passivation ability of PCBM/PCBDMAM double fullerene CBL toward perovskite layer and the improved J_{sc} and FF as well as the PCE enhancement of iPSC device.

Moreover, we evaluated the influence of PCBDMAM interlayer on the electron conductivity (σ_0) of iPSC devices based on PCBM/PCBDMAM double fullerene CBL and PCBM single CBL with the architectures of ITO/PCBM/PCBDMAM/Ag and ITO/PCBM/Ag. According to the following function:

$$I = \sigma_0 A L^{-1} V \tag{2}$$

Where A is area of the device, L is thickness of the films [33,62,63]. The higher σ_0 (7.96 \times 10^{-3} mS cm $^{-1}$) of device based on PCBM/PCBDMAM double fullerene CBL than that of device with only PCBM single CBL (3.04 \times 10^{-3} mS cm $^{-1}$) indicates the higher electron transport ability and less interfacial defect in the device with the aid of PCBDMAM interlayer (see Supporting Information S16 for detailed analysis). We further studied the influence of PCBDMAM interlayer on the electron



Fig. 4. (a) Stabilities of devices with and without PCBDMAM stored in ambient condition without encapsulation (temperature: 20 °C, relative humidity: ~35%) for 1440h. (b) Water contact angles on MAPbI₃/PCBM and MAPbI₃/PCBM/PCBDMAM. (c) Photographs of perovskite film of PCBM and PCBM/PCBDMAM after water was dropped on the surface for several minutes.

mobility of the iPSC device by space charge limited current (SCLC) measurements based on electron-only device with the configuration of ITO/TiO_x/perovskite/PCBM/PCBDMAM/Ag. Based on the Mott-Gurney equation (Supporting Information S17 for detailed analyses), the electron mobility (μ_e) of the device with PCBM/PCBDMAM double fullerene CBL was calculated to be 1.08×10^{-4} cm² V⁻¹ S⁻¹ which is higher than that of the control device with PCBM single CBL ($\mu_e = 4.52 \times 10^{-5}$ cm² V⁻¹ S⁻¹), suggesting the decreased non-radiative recombination at interface of perovskite and cathode as well as the reduced series resistance (R_s) which facilitate the increase of FF and J_{sc} (as shown in Table 1).

To unveil the charge transport dynamics of iPSC devices, we carried out the electrochemical impedance spectroscopy (EIS) measurements in dark under a reverse potential of 1.0 V. Fig. 3d compares the Nyquist plots of the iPSC devices with PCBM/PCBDMAM double fullerene CBL and single PCBM CBL and their corresponding fitted curves using an equivalent circuit model were also illustrated [64]. The fitted parameters obtained from Nyquist plots including series resistance (R_s), interface charge transfer resistance (Rct), and the constant phase element (CPE) are related to the interfacial ohmic contact and non-ideal chemical capacitances of the device, respectively (Summarized in Supporting Information Table S5). The iPSC device based on PCBM/PCBDMAM double fullerene CBL exhibits significantly lower R_s (13.19 Ω cm²) and R_{ct} (157.9 Ω cm²) than those of the control device with only PCBM single CBL with the value of R_s (27.53 Ω cm²) and R_{ct} (1081.1 Ω cm²), indicating the improved charge transport capability of iPSC device upon the involvement of PCBDMAM interlayer, which is beneficial to the J_{sc} and FF of the iPSC devices.

3.3. Stability of iPSC devices based on PCBM/PCBDMAM double fullerene CBL

We further evaluated the ambient stability of the iPSC devices by storing them without any encapsulation in dark under the ambient atmosphere (temperature: 20 °C, relative humidity: ~35%). As shown in Fig. 4a, the iPSC devices based on PCBM/PCBDMAM double fullerene CBL still retained approximately 67% of the initial PCE after 1440 h exposure. While the control device with single PCBM CBL only retained 43% of the initial PCE, indicating the improved device stability after inserting PCBDMAM interlayer. Moreover, the monitored photovoltaic parameters including V_{oc} , J_{sc} and FF of the devices during 1440 h storage are compared in Supporting Information Fig. S22. The improved ambient stability of the iPSC device based on PCBM/PCBDMAM double fullerene CBL was attributed to the improved hydrophobicity of PCBDMAM interlayer, which protects perovskite layer from the erosion of water and oxygen. Indeed, the improved hydrophobicity of PCBDMAM was confirmed by the larger water contact angle of 85.1° for $FTO/NiO_x/perovskite/PCBM/PCBDMAM$ film than that of $FTO/NiO_x/perovskite/PCBM$ film (74.6°, Fig. 4b). In order to verify the improved stability of iPSC device after incorporating PCBDMAM interlayer, water was dropped directly onto the $FTO/NiO_x/perovskite/PCBM$ films with and without PCBDMAM to observe visually the color change of perovskite film (Fig. 4c). Obviously, the color of MAPbI₃ perovskite film without PCBDMAM interlayer quickly changed from black to yellow within only 3 min, indicating the rapid decomposition of the perovskite. However, with the existence of PCBDMAM interlayer on PCBM, the MAPbI₃ perovskite film still keeps the pristine black color after 3 min and gradually turns into yellow color after 13 min, indicating the improved device stability.

4. Conclusions

In summary, a novel bis-dimethylamino-functionalized fullerene derivative (PCBDMAM) was synthesized via a facile esterification reaction, and corresponding molecular structure was confirmed by ¹H and ¹³C NMR, FT-IR spectroscopies, and MALDI-TOF mass spectrometry. PCBDMAM was applied as an auxiliary fullerene interlayer atop of PCBM to form a PCBM/PCBDMAM double fullerene CBL in MAPbI3 iPSC devices. Incorporation of PCBDMAM interlayer facilitates the formation of interfacial dipole layer between PCBM and Ag cathode, resulting in decrease of the work function of the Ag cathode. Consequently the interfacial energy offset between PCBM CBL and Ag cathode is minimized, facilitating electron transport from PCBM CBL to Ag cathode. As a result, iPSC devices based on PCBM/PCBDMAM double fullerene CBL exhibit the highest PCE of 18.11%, which is drastically higher than that of the control device based on single PCBM CBL (14.21%) and represents the highest value reported for double fullerene CBL-based iPSC devices. Moreover, due to the higher hydrophobicity of PCBDMAM than PCBM, iPSC devices based on PCBM/PCBDMAM double fullerene CBL shows an enhanced ambient stability, retaining more than 67% of the initial PCE after storage 1440 h exposure under the ambient atmosphere without any encapsulation, whereas only 43% retaining was achieved for the control device based on single PCBM CBL. With the effectiveness of double fullerene cathode buffer layers in enhancing both the efficiency and stability of iPSC devices, our strategy paves the way to realizing practical applications of PSCs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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