Acenaphthylene-imide based small molecules/TiO₂ bilayer as electron-transporting layer for solution-processing efficient perovskite solar cells

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ABSTRACT It is of great significance to design and synthesize highly efficient n-type organic small molecules as electron-transporting layer (ETL) materials to achieve high performance planar perovskite solar cells (PVKSCs) with low-temperature solution-processing. In this article, acenaphthylene-imide based small molecules AI1, AI2 and AI3 were developed with lower-lying LUMO energy levels and were further applied as non-fullerene ETL materials for solution-processed PVKSCs. When TiO₂/AIX bilayer was used as ETL, an average power conversion efficiency (PCE) of 15.0% was achieved for TiO₂/AI1 based PVKSCs with conventional configuration, while pristine TiO₂ based devices presented a PCE of 11.7% only. All the results demonstrate that acenaphthylene-imide derivatives could be promising ETL materials to accomplish low-temperature solution-processed high performance PVKSCs.

Keywords: acenaphthylene imide, electron transporting layer, perovskite solar cell, power conversion efficiency

INTRODUCTION

During the past five years, organic-inorganic hybrid perovskite solar cells (PVKSCs) as a most promising renewable energy resource, has raised wide interest in the field of photovoltaic because of their easy fabrication, low cost, facile solution processability and outstanding performance for efficiently converting sunlight into electricity [1–5]. Since then, the power conversion

efficiency (PCE) of PVKSCs devices has dramatically increased and is even comparable to that of the traditional inorganic solar cells based on single/poly-crystalline silicon and CuIn_{1-x}Ga_xSe₂ (CIGS) [6–7]. Recently, PVKSCs have reached a certified maximum PCE of 22.1% with a FTO/TiO₂/perovskite/PTAA/Au architecture [1,8–9].

Lately, planar-heterojunction PVKSCs have attracted increasing attention owing to their simple device architectures and promising potential for low-temperature solution-processed fabrication, especially in the case of large-scale roll-to-roll fabrication [10–17]. Generally, by employing different charge transporting layer materials, two kinds of device configurations, conventional configuration and inverted configuration are classified for PVKSCs fabrication [6,8]. For PVKSCs with conventional device configuration, the bottom transparent electrode and top metal electrode are employed as anode and cathode, respectively, and an electron transport layer (ETL) was inserted at the cathode/perovskite interfaces. However, transition-metal oxides, such as ZnO [18] and SnO₂ [19], which are extensively applied as ETL, usually require high-temperature annealing and complicated preparation procedures, thereby posing great challenges for mass production or flexible devices [20]. For high throughput manufacturing of PVKSCs with facile processability, organic small molecules as ETL materials or electron interfacial layer with superior low-temperature

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Scheme 1 Chemical structures for NI and AI derivatives.

and solution processing features are highly required [6,11].

In general, good ETL materials for PVKSCs should fulfill three requirements below, i) matched energy levels with that of perovskite layer for photovoltage improvement, ii) high charge mobility for photocurrent enhancement, and iii) low interfacial resistance for good interface contact and fill factor improvement [11]. To date, hole transport layer (HTL) materials have received considerable attention, and a large number of HTL materials have been developed, accompanied with continuous improvement of device performance and stability [6,21–23]. Nonetheless, there are only few efforts dedicated to the development of suitable ETL materials [6,24–29]. Therefore, significant attention has already been guided to explore new n-type organic semiconductors as ETL materials that can be solution-processed at low-temperature [27]. As a matter of fact, fullerene derivatives have been widely employed as organic ETLs; however, owing to their high production cost, difficult chemical structure modification and poor ambient stability, they are not the ideal candidates for practical application [11,28,30]. Furthermore, it is not easy to finely tune the lowest unoccupied molecular orbital (LUMO) energy level of fullerene derivatives. As a result, it is imperative to develop n-type non-fullerene ETL materials with appropriate energy levels for efficient electron extraction and cathode optimization [27]. Small molecular n-type organic semiconductors exhibit attractive features which render them as promising candidates for ETL materials, and the molecule energy levels and packing modes can be easily and finely tuned to accomplish appropriate optoelectronic properties. Besides, small molecule ETL materials possess well-defined molecular structure, high purity, low production cost and batch-to-batch reproducibility [28,31]. Moreover, the study of n-type non-fullerene small molecules as ETL materials for PVKSCs fabrication is relatively rare till now [6,12,15,24,27,32–35].

Acenaphthylene-imide (**AI**) shows similar structure to naphthalene imide (**NI**), and the difference is the other

side of naphthalene, for **AI**, is a di-one structure, while for **NI**, it is an anhydride structure (Scheme 1). Regarding the **NI** derivatives with asymmetric chemical structures we have reported before, the LUMO energy levels range from -3.90 eV to -4.15 eV [36]. However, it is reported that molecules with C_2 symmetry structure are favorable for ordered molecular packing and high charge mobility [37]. A few **AI** derivatives have been reported to show high charge mobility up to $0.12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [38–43].

Taking these into consideration, **AI1**, **AI2** and **AI3** with C_2 symmetry as the counterparts of **NI1–3** are proposed in this article (Scheme 1). Through condensation reaction, **AI** derivatives **AI1**, **AI2** and **AI3** are readily obtained, and the LUMO energy levels range from -3.76 to -4.05 eV. They display an excellent thermal stability with 5% weight loss over 410°C under nitrogen atmosphere. Furthermore, **AI1/AI2/AI3** are employed as ETL materials to fabricate regular PVKSCs, and when TiO_2/AIX bilayer is adopted as ETL, an average PCE of 15.0% was obtained for $\text{TiO}_2/\text{AI1}$ based devices.

EXPERIMENTAL SECTION

Materials and methods

Anhydrous toluene and tetrahydrofuran were freshly distilled after being processed with sodium and benzophenone under argon atmosphere prior to use. For devices fabrication, methylammonium iodide (MAI, 99.8%, Dyesol), formamidinium iodide (FAI, 99.8%, Dyesol), PbI_2 (99.999%, Alfa), PbCl_2 (99.999%, Alfa), N,N -dimethylformamide (DMF) (99.8%, Aladdin), isopropanol (IPA, 99.5%, Sigma-Aldrich), chlorobenzene (CB, 99.8%, Sigma) and [6,6]-phenyl C_{61} butyric acid methyl ester (PC_{61}BM , 98%, nano-c) were used as received without further purification.

^1H nuclear magnetic resonance (NMR) and ^{13}C NMR were measured by a Bruker Ultra Shield Plus AV400 spectrometer at 298 K in deuterated chloroform with solvent residual (CDCl_3 , $\delta=7.26$ ppm) as the internal standard. Matrix assisted laser desorption ionization

time-of-flight mass spectrometry (MALDI-TOF MS, Bruker Autoflex II) was recorded using anthracene-1,8,9-triol as the matrix. Differential scanning calorimeter (DSC) (Mettler DSC823e thermal analyzer) and thermal gravimetric analyzer (TGA) (Rigaku TG-DTA 8120 thermal analyzer) analysis were performed with a heating rate of $10^{\circ}\text{C min}^{-1}$ under nitrogen flow. UV-vis absorption and fluorescence spectra were recorded with a Shimadzu UV-1700 spectrometer and a RF-5301 fluorometer, respectively. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were tested by using CHI 620C electrochemical analyzer in tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 , 0.1 mol L^{-1} , in dry CH_2Cl_2), and ferrocene/ferrocenium (Fc/Fc^+) redox couple was used as an internal standard. Gold disc (diameter of 2 mm), Pt wire and Ag/AgCl electrode were used as working electrode, counter electrode and reference electrode, respectively.

Device fabrication

The device fabrication process is similar to our reported procedures [44]. Planar PVKSCs were fabricated on pre-patterned fluorine tin oxide (FTO) glass substrates (around $2 \text{ cm} \times 2.5 \text{ cm}$ in size, 7Ω per square). The FTO substrates were cleaned sequentially in detergent, deionized water, acetone, and ethanol in an ultrasonic bath for 20 min, respectively. Then, the FTO substrates were dried with N_2 and treated in a UV ozone oven for 20 min. The 0.15 and 0.30 mol L^{-1} compact TiO_2 layer precursor solutions were prepared by adding 73.2 and $146.4 \mu\text{L}$ titanium diisopropoxide bis(acetylacetonate) $75 \text{ wt\%}$ in IPA into 1-butanol (1 mL), respectively.

The spin-coating procedure for compact TiO_2 layer was conducted as below: first, the precursor solution (0.15 mol L^{-1}) was spin-coated on the FTO substrates at $4,000 \text{ rpm}$ for 45 s , then the substrates were annealed on a hotplate in air at 120°C for 5 min ; the same process was repeated twice with 0.3 mol L^{-1} titanium diisopropoxide bis(acetylacetonate) solution. As-prepared film was annealed at 450°C for 15 min . After the substrates cooled down to room temperature, the TiO_2 -covered substrates were immersed into TiCl_4 aqueous solution (40 mmol L^{-1}) at 70°C for 45 min and annealed at 450°C for 15 min . Then the samples were transferred into glove-box and spin-coated with sample (5 mg mL^{-1}) or PC_{61}BM solution (10 mg mL^{-1} in CB) at $6,000 \text{ rpm}$ for 45 s , followed by heating at 100°C for 5 min . To make a uniform perovskite layer, PbI_2 (1.36 mol L^{-1}) and PbCl_2 (0.24 mol L^{-1}) were dissolved in DMF and stirred for 2 h at 75°C . MAI (70 mg) and FAI (30 mg) were dissolved in

IPA (1 mL) with additional DMF ($10 \mu\text{L}$). After that, PbX_2 precursor solution was spin-coated on the top of the sample covered substrates at $3,000 \text{ rpm}$ for 45 s , and then the solution of MAI and FAI was spin-coated on top of the PbX_2 substrates at $3,000 \text{ rpm}$ for 45 s . The samples were annealed at 100°C for 10 min on hotplate. During the annealing process, IPA ($40 \mu\text{L}$) was added around the substrates. Next, $2,2',7,7'$ -tetrakis[N,N -di(4-methoxyphenyl)amino]-9,9'-spiro-bifluorene (spiro-OMeTAD) solution was spin-coated onto the perovskite layer at a rate of $4,000 \text{ rpm}$ for 45 s , where spiro-OMeTAD (90 mg mL^{-1} in CB) precursor solution was employed with addition of lithium bis(trifluoromethylsulfonyl) imide (Li-TFSI) in acetonitrile ($45 \mu\text{L}$ 170 mg mL^{-1}), FK209 in acetonitrile ($75 \mu\text{L}$ 100 mg mL^{-1}) and 4-*tert*-butylpyridine ($10 \mu\text{L}$). Finally, Ag layers (100-nm -thick) were thermally evaporated as the top electrodes. The area of the device was 0.075 cm^2 defined by shadow masks.

Synthesis

2-(2-Octyldodecyl)-1,3-dioxo-2,3-dihydro-1H-pyrido [3',4',5':5,6]acenaphtho[1,2-b]quinoxaline-7,10-dicarbonitrile (AII)

In a 100 mL two necked-flask, **2** (92.0 mg , 0.58 mmol), **9** (319.0 mg , 0.60 mmol , 1 eq.) and acetic acid (10 mL) was added. Then the reaction was reflux under nitrogen atmosphere for 12 h . Then it was cooled to room temperature, extracted with ethyl acetate (EtOAc) (200 mL), and washed with brine several times. After removal of all solvents, the oil material was purified with column chromatography ($\text{EtOAc}:\text{PE} = 1:10$) to get crude material. The crude product was recrystallized from methanol (MeOH) three times to get pure **AII** as light-yellow solid (246.5 mg , 65%). ^1H NMR (400 MHz , CDCl_3), δ (ppm) = 8.77 (d, 2H , $J = 7.2 \text{ Hz}$), 8.70 (d, 2H , $J = 7.6 \text{ Hz}$), 8.21 (s, 2H), 4.16 (d, 2H , $J = 7.2 \text{ Hz}$), $2.04\text{--}1.95$ (m, 1H), $1.41\text{--}1.21$ (m, 32H), $0.87\text{--}0.82$ (m, 6H). ^{13}C NMR (100 MHz , CDCl_3), δ (ppm) = 163.19 , 156.85 , 156.74 , 141.10 , 134.51 , 134.35 , 132.65 , 125.72 , 125.14 , 124.91 , 118.10 , 114.88 , 44.92 , 36.84 , 31.93 , 31.69 , 30.07 , 29.66 , 29.58 , 29.37 , 29.31 , 26.50 , 22.69 , 14.16 . MALDI-TOF MS (m/z) calcd. for $\text{C}_{46}\text{H}_{48}\text{N}_5\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 654.381 , found 654.437 .

2-(2-Octyldodecyl)-1,3-dioxo-2,3-dihydro-1H-pyrido [3',4',5':5,6]acenaphtho[1,2-b]quinoxaline-8,9-dicarbonitrile (AI2)

To a solution of **9** (297.0 mg , 0.54 mmol) and acetic acid (10 mL), **4** (85.0 mg , 0.53 mmol , 1 eq.) was added under

N_2 . After it was stirred for 12 h at 135°C, the reaction was cooled to room temperature and extracted with EtOAc (200 mL). The organic layer was washed with brine (3×100 mL). The solvent was removed under reduced pressure, and the oil material was purified with column chromatography using (EtOAc:PE = 1:15) to get crude material. Then it was recrystallized from MeOH three times to obtain pure **AI2** as yellow-greenish solid (155.9 mg, 45%). 1H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.79 (d, 2H, J = 7.6 Hz), 8.68 (s, 2H), 8.62 (d, 2H, J = 7.2 Hz), 4.16 (d, 2H, J = 7.6 Hz), 1.99 (m, 1H), 1.41–1.21 (m, 32H), 0.86–0.82 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) = 163.18, 157.40, 142.19, 137.12, 136.19, 134.63, 132.74, 125.71, 125.25, 124.48, 114.83, 114.70, 44.91, 36.79, 31.92, 31.89, 31.67, 30.04, 29.64, 29.58, 29.35, 29.31, 26.47, 22.69, 22.67, 14.13. MALDI-TOF MS (m/z) calcd. for $C_{46}H_{48}N_5O_2$ ($M+H$)⁺ 654.381, found 654.437.

2-(2-Octyldodecyl)-1,3-dioxo-2,3-dihydro-1H-pyrazino
[2',3':2,3]indeno[6,7,1-def]isoquinoline-7,8-dicarbonitrile
(**AI3**)

A mixture of 2,3-diaminomaleonitrile (**10**) (60.5 mg, 0.56 mmol) and **9** (307.0 mg, 0.56 mmol) was dissolved in acetic acid (10 mL). Then it was stirred for 12 h at 135°C and then cooled to room temperature. The reaction was extracted with EtOAc (200 mL) and washed with brine (3×100 mL). The solvent was removed under reduced

pressure, and the oil material was purified with column chromatography using (EtOAc:PE = 1:12) to get the crude material. The crude product was recrystallized from MeOH three times to get pure **AI3** as bright green solid (147.0 mg, 43.5%). 1H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.77 (d, 2H, J = 7.6 Hz), 8.63 (d, 2H, J = 7.2 Hz), 4.14 (d, 2H, J = 7.2 Hz), 1.97 (m, 1H), 1.40–1.20 (m, 32H), 0.87–0.82 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) = 162.89, 155.75, 133.69, 132.87, 132.64, 130.98, 126.85, 126.78, 125.04, 113.51, 44.36, 36.84, 31.92, 31.89, 31.64, 30.03, 29.64, 39.57, 39.35, 39.31, 26.44, 22.70, 22.67, 14.14. MALDI-TOF MS (m/z) calcd. for $C_{38}H_{46}N_5O_2$ ($M+H$)⁺ 604.365, found 604.389.

RESULTS AND DISCUSSION

The synthetic route for **AI1**, **AI2** and **AI3** is illustrated in Scheme 2. *Ortho*-diamine **2** and **4** are synthesized according to the reported procedures, by reducing thiadiazole **1** and **3** with iron powder in acetic acid [45]. Through double Friedel-Crafts reaction in refluxing chlorobenzene for 48 h, **5** was easily converted to compound **6**, followed by hydrolysis in HCl (aq) and dehydration in acid anhydride, and **7** was obtained with excellent yield [43]. Later 2-octyldodecan-1-amine was introduced onto **7** to facilitate further purification and increase the processability, and **8** was yielded in ethanol with a yield of 62% [46]. By taking CrO_3 as the oxidant to oxidize **8**, the di-one **9** was synthesized with only 18%

Scheme 2 The synthetic route for **AI1**, **AI2** and **AI3**.

Figure 1 Normalized UV-vis absorption spectra for (a) **AI1**, (b) **AI2** and (c) **AI3** in CHCl_3 and drop-casted film; (d) cyclic voltammograms of **AI1**, **AI2** and **AI3** in dry dichloromethane with a scan rate at 50 mV s^{-1} .

yield. The small molecular acceptor **AI1**, **AI2** and **AI3** were readily achieved with excellent yield *via* condensation reaction between di-one **9** and *ortho*-diamine **2**, **4** and **10**, respectively [45]. **AI1**, **AI2** and **AI3** all showed good solubility in various organic solvents, such as DCM, chloroform and toluene. Additionally, NMR spectroscopy (^1H NMR, ^{13}C NMR) and MALDI-TOF mass spectrometry (MS) were applied to identify the chemical structures and purity of all the molecules (see Experimental section and Supporting information).

The UV-vis absorbance of **AI1**, **AI2** and **AI3** are shown in Fig. 1a–c, and well-resolved UV-vis absorption bands can be clearly observed with the longest absorption maximum ($\lambda_{\text{ab}}^{\text{max}}$) locating at 402, 404 and 393 nm in chloroform solution, and 415, 416 and 403 nm in film for **AI1**, **AI2** and **AI3**, respectively. The three molecules show a red-shift of about 10 nm in the solid state, suggesting a favorable intermolecular π - π stacking in thin film. The respective lowest energy absorption edge (λ_{opt}) determined from UV-vis absorption in film for **AI1**, **AI2** and **AI3** was 433, 476, and 440 nm; Thus the optical energy gap ($E_{\text{g}}^{\text{opt}}$) was calculated to be 2.85, 2.67 and 2.79 eV for **AI1**, **AI2** and **AI3**, respectively, following the equation $E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{onset}}$ (Table 1) [47,48].

To understand the electrochemical behaviors of the three molecules, CV and differential pulse voltammetry (DPV) was carried out in dichloromethane (Fig. 1d, Fig. S3). As illustrated in Fig. 1d, four quasi-reversible reductions could be clearly observed for **AI1** with onset reduction potential $E_{\text{red}}^{\text{onset}}$ at -1.04 V . For **AI2**, there are five quasi-reversible reduction waves with $E_{\text{red}}^{\text{onset}}$ at

-0.99 V . However, only two quasi-reversible reduction waves were recorded for **AI3** with $E_{\text{red}}^{\text{onset}}$ at -0.77 V . In addition, upon oxidation even up to 1.80 V , we cannot observe any obvious redox waves. The LUMO energy level of **AI1**, **AI2** and **AI3** calculated from $E_{\text{red}}^{\text{onset}}$ is -3.76 , -3.81 and -4.03 eV , respectively. Therefore, the HOMO energy levels of **AI1**, **AI2** and **AI3** are determined to be -6.61 , -6.48 and -6.82 eV , according to the equation $\text{HOMO} = \text{LUMO} - E_{\text{g}}^{\text{opt}}$ [49–51]. In contrast to **NI** derivatives **NI1**, **NI2** and **NI3** reported, the change of LUMO energy level is 0.24, 0.09 and 0.12 eV for **AI1**, **AI2** and **AI3**, respectively (Table S2, Fig. S2). Compared with **AI1** and **AI2**, there is one phenyl ring missing for **AI3**, and the LUMO energy level was lowered by 0.27 and 0.22 eV, respectively. The low-lying LUMO energy levels of all materials suggest that they are potential candidates for air stable ETL materials for PVKSCs.

To further understand the position effect of $-\text{CN}$ group on the molecular electronic structures, the electron density distribution and the molecular architecture fundamentals of **AI1**, **AI2** and **AI3** were theoretically investigated by density functional theory (DFT) calculation at the B3LYP/G-31G(d,p) levels. The long alkyl chain on the imide was replaced by methyl units to simplify the simulation, and Fig. 2 shows the simulated HOMO/LUMO orbital distribution and the calculated energy levels of **AI1**, **AI2** and **AI3**. The green color represents positive electrostatic potential, while the red stands for the negative one. As shown in Fig. 2, all materials show high coplanarity, which is beneficial for charge transport. For **AI1** and **AI2**, HOMO is delocalized on the molecule backbone, whereas LUMO is mainly localized on the acenaphthylene unit. However, both LUMOs and HOMOs are delocalized over the entire molecule backbone for **AI3**. The calculated HOMO/LUMO and energy bandgaps were summarized in Table 1, and for **AI1**, **AI2** and **AI3**, the calculated LUMO/HOMO energy levels were $-3.53/-7.05$, $-3.65/-7.15$ and $-3.95/-7.49 \text{ eV}$, respectively. The calculated bandgap for **AI1**, **AI2** and **AI3** was very close, 3.52 eV for **AI1**, 3.50 eV for **AI2**, and 3.54 eV for **AI3**.

The thermal behaviors of **AI1**, **AI2** and **AI3** in solid-state were investigated by both TGA and DSC techniques. As observed from the TGA measurements, all **AI1**, **AI2** and **AI3** show great thermal stability with 5% weight loss over 410°C under nitrogen atmosphere (Fig. 3a). This high thermal stability ensures their potential application for PVKSCs. The DSC curves for **AI1**, **AI2** and **AI3** are shown in Fig. 3b–d. For **AI1**, the DSC curve shows two

Table 1 Photophysical properties for **AI1**, **AI2** and **AI3**

Cpd	λ_{ab}^{max} (nm)		E_g^{opt} (eV)	E_{red}^{onset} (V)	HOMO ^b (eV)	LUMO ^c (eV)	HOMO ^d (eV)	LUMO ^d (eV)	E_g^d (eV)
	Solution	Film							
AI1	347, 386, 402	339, 415	2.85	-1.04	-6.61	-3.76	-7.05	-3.53	3.52
AI2	343, 382, 404	333, 416	2.67	-0.99	-6.48	-3.81	-7.15	-3.65	3.50
AI3	330, 372, 393	384, 403	2.79	-0.77	-6.82	-4.03	-7.49	-3.95	3.54

a) E_g^{opt} was estimated from the lowest-energy absorption edge in film. b) HOMO was determined according to the equation $HOMO = LOMO - E_g^{opt}$. c) LUMO was calculated according to the equation $LUMO = -(4.80 + E_{red}^{onset})$ [19] in which E_{red}^{onset} is the onset potential of the first wave, 4.80 eV is the energy level of ferrocene/ferrocenium (Fc^+/Fc) below the vacuum level. d) Calculated by the B3LYP/6-31G(d,p) basis set.

Figure 2 Molecular orbital amplitude plots of HOMO/LUMO energy levels of **AI1**, **AI2** and **AI3** (long alkyl chains were substituted with methyl units) calculated by the B3LYP/6-31G(d,p) basis set. **Figure 3** Thermal behaviors of **AI1**, **AI2** and **AI3**. (a) TGA curves for **AI1**, **AI2** and **AI3** with a heating rate of $10^\circ\text{C min}^{-1}$. DSC curves for (b) **AI1**, (c) **AI2**, and (d) **AI3** with a heating-cooling scan rate of $10^\circ\text{C min}^{-1}$ under nitrogen.

endothermic transitions at 195°C and 211°C upon heating, and two exothermic transitions at 166°C and

75°C upon cooling (Fig. 3b). And the DSC curve of **AI2** exhibits one endothermic peak at 198°C and two exothermic peaks at 167°C and 160°C upon cooling (Fig. 3c). However, the DSC curve for **AI3** only shows one endothermic transition at 144°C , and one exothermic transition at 103°C (Fig. 3d). In comparison with NI derivatives, the DSC results indicate that **AI1** and **AI2** are probably liquid crystal materials [36]. The electron mobilities of **AIX** were evaluated by using electron-only devices with the structure of ITO/PEIE/**AIX**/Ca/Ag ($X=1,2,3$), as shown in Fig. S4. The electron mobility of **AIX** can be estimated from the J - V curves in Fig. S4b by the Mott-Gurney equation as following: $J = (8/9)\mu\epsilon_0\epsilon_r(V^2/L^3)$, where the J is current density, μ is the electron mobility, ϵ_0 is vacuum permittivity ($\epsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$), ϵ_r is the dielectric permittivity of **AIX** (~ 3), V is the applied voltage and L is the thickness of **AIX** layer ($\sim 90 \text{ nm}$). The estimated electron mobility of **AI1**, **AI2** and **AI3** were 9.10×10^{-4} , 4.88×10^{-4} , and $4.64 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively.

In the following study, in order to simplify the PVKSCs device fabrication process and avoid the deposition problem, TiO_2 /**AIX** bilayer as an appropriate ETL choice was used. In this case, metal oxide TiO_2 could solve the imperfect coverage problem caused by the dissolution of **AIX** in DMF solvent. Similar to previously reported TiO_2 /PCBM bilayer, both TiO_2 and ETL together acted as the ETL [52–55]. The device configuration is shown in Fig. 4a, and the device performance investigated under 100 mW cm^{-2} air mass 1.5 global (AM 1.5G) illumination is summarized in Table 2 and the current density-voltage (J - V) curves are shown in Fig. 4b. The pristine TiO_2 only presented a PCE of 11.7%. While when TiO_2 /**AI1**, TiO_2 /**AI2** and TiO_2 /**AI3** (concentration, 5 mg mL^{-1}) were applied as ETLs, the average PCE achieved were 15.0%, 12.8% and 12.1%, respectively, which is apparently higher than that from pristine TiO_2 (Table 2). Especially for TiO_2 /**AI1** ETL, the champion PVKSC devices exhibited an enhanced J_{sc} of 22.9 mA cm^{-2} and FF of 0.71 with

Figure 4 (a) The device configuration of PVKSCs device with TiO_2 as hole blocking layer. (b) J - V characteristics of the devices based on different ETLs. (c) The best device based on $\text{TiO}_2/\text{AI1}$ ETL. (d) IPCE spectra of the devices based on different ETLs.

Table 2 Photovoltaic parameters of PVKSCs with different ETLs (TiO_2 as hole blocking layer). The average results are derived from 12 perovskite solar cells.

ETL	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
TiO_2	0.93 ± 0.04	21.4 ± 0.5	0.52 ± 0.05	11.7 ± 0.4
$\text{TiO}_2/\text{AI1}$	0.95 ± 0.03	22.8 ± 0.3	0.69 ± 0.02	15.0 ± 0.3
$\text{TiO}_2/\text{AI2}$	0.91 ± 0.02	22.4 ± 0.2	0.63 ± 0.03	12.8 ± 0.3
$\text{TiO}_2/\text{AI3}$	0.88 ± 0.02	22.0 ± 0.02	0.64 ± 0.02	12.1 ± 0.2

similar V_{oc} of 0.98 V, which significantly improved the device PCE to 16.0% (Fig. 4c). The film thicknesses were also optimized by using different concentrations of small molecules (Table S3). For comparison, TiO_2/PCBM was also investigated as ETL, and the PCE obtained was 15.5%. The PCE from $\text{TiO}_2/\text{AI1}$ based PVKSCs is similar with that from TiO_2/PCBM , but higher than that from pristine TiO_2 only. The incident photon-to-electron conversion efficiency (IPCE) spectra of the corresponding devices were measured, and the integrated current densities were 20.7, 21.9, 21.7 and 20.8 mA cm^{-2} for TiO_2 , $\text{TiO}_2/\text{AI1}$, $\text{TiO}_2/\text{AI2}$, and $\text{TiO}_2/\text{AI3}$, respectively (Fig. 4d). The good photon-to-electron conversion ensures the high current density of the devices.

In addition, PVKSC devices employing **AI1**, **AI2** and **AI3** layer only as ETLs with a conventional configuration were also fabricated (Fig. S5, Table S4). Without using any materials for ETL, the PCE was 6.5% only, and PVKSC devices taking **AI1** and **AI2** as ETL showed respective PCE of 4.8% and 7.2%. Among the three molecules, devices based on **AI3** showed the best PCE performance of 8.9%, with V_{oc} of 0.94 V, J_{sc} of 16.2 mA cm^{-2} , and FF of 0.58. The relatively low performance is probably contributed to the single ETL layer which might be partly destroyed when depositing the PbI_2 layer in DMF, and hence, deteriorated the electron-transporting behaviors.

The hysteresis curves of the devices were also checked by scanning the device along forward (from short-circuit to open-circuit) and reverse (from open-circuit to short-circuit) direction (Fig. 5). Similar to TiO_2/PCBM , the bilayer TiO_2/AIX ETL reduced the hysteresis behavior, compared to the large hysteresis of pristine TiO_2 based devices. The steady-state PCE output of the devices with $\text{TiO}_2/\text{AI1}$ ETL was also performed, and PCE was enhanced from 10.7% (TiO_2) to 15.4% ($\text{TiO}_2/\text{AI1}$). Devices with $\text{TiO}_2/\text{AI2}$, and $\text{TiO}_2/\text{AI3}$ ETLs exhibited

Figure 5 Hysteresis curves and steady-state current output at maximum power point of PVKSCs based on (a, b) TiO_2 and (c, d) $\text{TiO}_2/\text{AI1}$ as ETLs.

Figure 6 (a) Steady-state PL spectra of perovskite films deposited on different ETLs. (b) Time-resolved PL spectra of perovskite films deposited on different ETLs.

similar results (Fig. S6).

The charge transfer efficiency of TiO_2/AIX bilayer ETL was studied by steady-state photoluminescence (PL) and time-resolved PL. As shown in Fig. 6, the steady-state PL exhibited a significant reduction in PL intensity, indicating an efficient charge transfer process occurred between ETL and perovskite layer. The charge transfer dynamics at the perovskite/ETL interface was further studied by time-resolved PL. As shown in Fig. 6b, the PL lifetimes were fitted by bi-exponentially function. For perovskite film deposited on glass substrate, the PL lifetime is much longer around 732 ns. The PL lifetimes significantly decreased to 26.0, 56.5, 33.2 and 11.8 ns for the perovskite films deposited on TiO_2 , $\text{TiO}_2/\text{AI1}$, $\text{TiO}_2/\text{AI2}$, and $\text{TiO}_2/\text{AI3}$, respectively. It was found that the PL lifetime was slightly larger for $\text{TiO}_2/\text{AI1}$ based system, which might be due to the surface trap passivation effect [11]. It has been reported that passivation of the perovskite surface could effectively enhance PL lifetimes owing to diminished nonradiative recombination [56].

Figure 7 Normalized (a) PCE, (b) J_{sc} , (c) V_{oc} , and (d) FF of un-encapsulated PVKSC devices based on different ETLs as a function of storage time under air ambient condition at room temperature and 40% relative humidity.

The device stability is an important issue for PVKSCs due to the chemical instabilities towards water and light. The stability measurement was investigated by storing the un-encapsulated devices under air ambient conditions (with a relative humidity of 60%) for 96 h. As can be seen from Fig. 7, compared to bare TiO_2 with PCE decayed to 51%, the TiO_2/AIX bilayer ETL could significantly enhance the stability, and PCE still retained 74%, 82% and 86% for devices with $\text{TiO}_2/\text{AI1}$, $\text{TiO}_2/\text{AI2}$, $\text{TiO}_2/\text{AI3}$ as ETLs, respectively. The decreased PCE was mainly contributed to the J_{sc} decrement. The slightly increased V_{oc} may be caused by improved interface contact between ETL and perovskite layer during the aging process. Nevertheless, the device with AIX/TiO_2 bilayer ETL exhibited improved air stability compared to that with bare TiO_2 .

CONCLUSIONS

In summary, acenaphthylene-imide based small molecules **AI1**, **AI2** and **AI3** have been synthesized with LUMO energy levels lowered to -4.03 eV. The theoretical simulation of energy levels was in accordance with the cyclic voltammetry results. And **AI1**, **AI2** and **AI3** show a high thermal stability with 5% weight loss over 410°C under N_2 atmosphere. All **AI1**, **AI2** and **AI3** were further used as non-fullerene ETL materials for solution-processed PVKSCs with conventional configuration. When TiO_2/AIX bilayer was employed as ETL, $\text{TiO}_2/\text{AI1}$ based devices show an average PCE of 15.0%, and a best PCE performance of 16.0%, while pristine TiO_2 and

TiO₂/PCBM based devices present a PCE of 11.7% and 15.5%, respectively. All the results demonstrate that acenaphthylene-imide derivatives could be used as potential ETL materials to achieve solution-processed high-performance PVKSCs, and highly-efficient organic non-fullerene ETL materials need further development in the future.

Received 9 June 2018; accepted 9 August 2018;
published online 6 September 2018

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Acknowledgements The work was supported by the National Natural Science Foundation of China (61604071, 61525402, 61604119, 61704131 and 61775095), Natural Science Foundation of Jiangsu Province (BK20161012), Postgraduate Research & Practice Innovation Program of Jiangsu Province (SJZZ16_0139) and SICAM Scholarship (38600001).

Author contributions Shao J and Shi N synthesized and characterized the materials, and wrote the manuscript. Guo X and Lin Z fabricated the device and analyzed the results. Liu S and Zhao B calculated the molecule energy levels. Chang J, Shao J, and Dong X supervised the project and revised the manuscript. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Detailed synthetic procedures and ^1H NMR and ^{13}C NMR spectra. Normalized UV-vis absorption spectra, and the energy levels for **AI1**, **AI2**, **AI3**, **NI1**, **NI2**, and **NI3**. Photovoltaic parameters of PVKSCs with different electron transporting layers and different concentration (Table S3). These materials are available in the online version of the paper.

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基于茚烯酰二亚胺小分子/二氧化钛双分子电子传输层的高效钙钛矿太阳能电池

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摘要 设计合成高效n型小分子半导体作为钙钛矿太阳能电池的电子传输层对实现低温、可溶液加工的钙钛矿太阳能电池具有重要意义. 本文合成了三个低LUMO能级、基于茚烯酰二亚胺的小分子受体材料**AI1**, **AI2**, **AI3**, 系统表征了其光物理性质及电化学、热力学性质, 研究了其在钙钛矿太阳能电池器件中的应用. 当使用TiO₂/**AI1**作为电子传输层时, 钙钛矿太阳能电池的平均光电转换效率为15%, 比单独TiO₂电子传输层11.7%的平均光电转换效率有较大提升, 表明基于茚烯酰二亚胺的小分子**AI1**, **AI2**, **AI3**是良好的电子传输层材料, 可实现低温、可溶液加工的高效钙钛矿太阳能电池.