A novel perylene diimide-based zwitterion as the cathode interlayer for high-performance perovskite solar cells

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Perovskite solar cells (PSCs) have earned widespread and intense interest because of their excellent device performance. However, the existence of poor interface contacts and energy losses in the device are key challenges for the development of the PSCs in the future. In this work, we developed a novel perylene diimide-based zwitterion (QAPDI) as a cathode interlayer to improve the device performance of inverted PSCs. QAPDI exhibits excellent solubility, appropriate energy levels, and high electron mobility, suggesting that it is a suitable interlayer engineering material in inverted PSCs. The use of QAPDI as a cathode interlayer between the PCBM layer and metal electrode could improve the interface contact and reduce the energy level barrier, thus facilitating efficient electron injection and transport. Moreover, the application of QAPDI could obstruct the permeation of moisture into the perovskite film to reform the device stability. As a consequence, the optimal QAPDIbased device efficiency reached 20.55% together with enhanced device stability compared with that of the control device (18.6%). This work provides an excellent alternative cathode interlayer material for high-performance inverted PSCs.

1. Introduction

Perovskite materials have broad application prospects in the field of optoelectronic materials due to their advantages such as high molar extinction coefficient, double carrier transport, and long exciton lifetime.¹⁻³ By employing the high-efficiency perovskite materials to fabricate third-generation solar cells, the device efficiency increased from 3.8% to 25.2%, which fully illustrates that there is great potential for the development of perovskite solar cells (PSCs).⁴⁻⁶ However, device efficiency, stability, and large-area fabrication are three key issues that need to be resolved for the commercialization of the PSCs. Usually, the device structure of the PSCs is composed of two electrodes, an active layer of perovskite material, and two carrier transport layers. Due to the differences in compatibility and energy levels between the layers, this could lead to poor interface contacts and the presence of larger energy level barriers, resulting in increased energy losses and charge recombination in the devices, accompanied by decreased device efficiency and stability.⁷⁻¹⁴ Therefore, the development of effective interlayer engineering materials can effectively solve the above challenges.

In contrast with the conventional structure, the inverted PSCs have advantages in terms of flexibility and full solution-processing. However, there are poor interface contacts and increased energy losses between the electron transport layer and the metal electrode, which is a great obstacle for the development of the inverted PSCs.¹⁵⁻¹⁶ Usually, calcium,¹⁷ barium,¹⁸ and metal salts (for example, LiF and BaF₂)¹⁹ can be used as the cathode interlayer to modify the metal electrode, but the use of high vacuum fabrication increases the production cost of the device. In addition, calcium and barium are easily oxidized, and metal salts are easily degraded by moisture. These defects could greatly reduce the stability of the PSCs. Metal oxides (for example, TiO₂ and ZnO)^{20, 21} represent a better alternative, but their need for high-temperature thermal annealing is the limitation for large-scale device fabrication. Based on the above discussion, the development of organic interlayer engineering materials could further solve these problems. Compared with polymers, organic small-molecular materials show some advantages of easy structure determination, low cost, easy purification, and large-scale production.^{22, 23} They would be expected to be the best substitutes for the above interlayer materials. Based on the inverted PSCs, BCP (2,9-dimethyl-4,7diphenyl-1,10-phenanthroline)^{24, 25} and Bphen (4,7-diphenyl-1,10phenanthroline)^{26, 27} are utilized as two kinds of effective buffer layers, but the determined molecular energy levels lead to the existence of energy level barriers in the device, which is not conducive to electron injection. Other novel organic smallmolecular cathode interlayer materials can efficiently enhance the device performance and stability, which is beneficial to the development of the photovoltaic field.²⁸⁻³² Furthermore, the organic small-molecular interlayer engineering material containing a zwitterionic molecular skeleton could achieve good ohmic contact between the layers. If it has the suitable energy levels at the same time, a better energy level gradient can be achieved for facilitating electron injection. Therefore, we intend to develop organic smallmolecular interlayer engineering materials with dipolar interface property and suitable energy levels to optimize the device performance.

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Among the n-type semiconductor materials, perylene diimide derivatives have attracted great attention in the field of semiconductor materials due to their advantages of easy chemical modification, high electron affinity, high electron mobility, and good chemical stability.³³⁻³⁵ Therefore, compared to previous work, we have developed a novel perylene diimide derivative, namely QAPDI, as a cathode interlayer for the PSCs with the following advantages. (1) The shorter synthetic routes and higher yields are conducive to reducing the costs; (2) due to the introduction of the quaternary ammonium salt and herringbone side chains, QAPDI shows good solubility in the polar and nonpolar solvents, which facilitates solution processing and film preparation; (3) the existence of large conjugated skeleton guarantees high electron mobility, which could improve the electron transport performance in the device; (4) QAPDI shows suitable energy levels, which match the energy levels of perovskite (MAPbI₃) and PCBM, thereby reducing the energy level barrier and enhancing the electron injection; (5) large conjugated skeleton and zwitterionic structure can establish an excellent dipolar molecular framework, which is beneficial for the formation of a dipolar interface to achieve ohmic contact between the layers. Furthermore, the formed dipole interface can enhance the built-in voltage, and the electric field caused by the dipolar interface is superposed upon the original built-in electrical field in the devices, which could improve the electron transport and collection. Based on the above advantages, we hope that QAPDI could have a positive impact on the device efficiency and stability to achieve high-performance PSCs.

Herein, QAPDI was developed by three-step reactions in a high yield, and it exhibits suitable energy levels (LUMO = -3.99 eV and HOMO = -5.84 eV) and high electron mobility $(1.05 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$, which indicates that QAPDI could be utilized as a potential interlayer engineering material for inverted PSCs. Owing to the enhanced electron injection, reduced energy losses, and improved interface contacts, the optimal device efficiency increased from 18.6% for the Bphen-based device to 20.55% for the QAPDI-based device, which is attributed to the excellent improvement of the device parameters such as short-circuit current density (J_{sc}), opencircuit voltage (Voc), and fill factor (FF). What is more, efficient interlayer engineering could strengthen the film coverage on the PCBM layer and inhibit the permeation of moisture into the perovskite film, thereby improving the device stability. This work suggests that QAPDI can become an excellent alternative interlayer for future inverted PSCs.

2. Results and discussion

The synthesis and methodology of QAPDI are displayed in Scheme S1 and Supporting Information. QAPDI is synthesized by the bromination, amination, and quaternization reactions with a 36% total yield. Such a simple efficient synthetic route and methodology are beneficial to realize the commercial production of QAPDI. The design idea of the molecular skeleton is as follows. Firstly, the conjugated skeleton (perylene diimide unit) of QAPDI provides suitable energy levels and high electron mobility. Secondly, the herringbone side chain provides a guarantee of high solubility in the nonpolar solvents and promotes the distortion of the conjugated framework to reduce intermolecular aggregation. Thirdly, the quaternary ammonium salt increases the molecular polarity, thereby realizing the generation of a zwitterionic structure and increasing the solubility in the polar solvents. As a result, QAPDI is soluble in almost all common organic solvents, for instance, chloroform, toluene, chlorobenzene, methanol, ethanol, 2-butanol, dimethylformamide and dimethyl sulfoxide. Among them, the solubility in methanol, 2-butanol, and chloroform are higher than 15 mg mL⁻¹, indicating that excellent solubility is very important for the device fabrication. The molecular structures of intermediate and QAPDI were characterized by NMR and HRMS as depicted in Figures S1-S6.

The UV-Vis spectra of QAPDI were characterized in dichloromethane and the thin film. Figure 1a shows two absorption maxima at 561 nm in solution and 567 nm in the thin film, respectively, suggesting that the maximum absorption peaks were only red-shifted by 6 nm due to the weaker intermolecular aggregation. Then, the optical bandgap (E_q) was estimated to be 1.85 eV. Cyclic voltammetry (CV) was adopted to estimate the electrochemical properties of QAPDI as depicted in Figure 1b. The CV trace of QAPDI exhibits two pairs of reversible reduction peaks and three pairs of oxidation peaks, which are attributed to the perylene diimide core and the quaternary ammonium salt group. The lowest unoccupied molecular orbital (LUMO) level of QAPDI was estimated to be -3.99 eV in terms of the onset reduction potential (-1.09 V), which is very close to those of MAPbI₃ (-3.90 eV) and PCBM (-3.90 eV). This result suggests that the appropriate LUMO level makes it easy to achieve efficient electron injection and to reduce the energy level barrier between the layers. Moreover, the highest occupied molecular orbital (HOMO) level of QAPDI was estimated to be -5.84 eV according to the onset oxidation potential.

The current density-voltage (*J-V*) traces of electron-only devices were tested to estimate the electron mobilities of PCBM and QAPDI on the basis of the space charge limited current (SCLC) method. The SCLC device architecture is ITO/ZnO/active layer/Ca/Al. As depicted in Figure 1d, the electron mobility of QAPDI was calculated to be 1.05×10^{-3} cm² V⁻¹ s⁻¹, which is comparable to that of PCBM (1.21×10^{-3} cm² V⁻¹ s⁻¹). This indicates that QAPDI could be employed as a potential electron transport material, which could strengthen the directional movement of carriers and prevent charge recombination. Overall, QAPDI shows excellent solubility, appropriate energy levels, and high electron mobility, so it could be used as an interlayer engineering material to enhance the device performance.

To explore the effect of QAPDI as a cathode interlayer on the device performance, we fabricated the inverted PSCs possessing the device architecture of ITO/PTAA/PMMA/MAPbl₃/PCBM/Bphen or QAPDI/AI. The Bphen-based devices were employed as control devices. Figures 1c and 1e show the molecular structure of QAPDI and the device structure, respectively, and the energy levels of materials are also displayed in Figure 1f. The energy levels of four materials (MAPbl₃, PCBM, Bphen, and QAPDI) were measured by the ultroviolet photoelectron spectrometer (UPS) method, and the results are summarized in Table S1. The UPS spectra of the four materials are shown in Figure S7. As a result, the UPS and CV results show the same trend. The UPS results reveal that the energy level diagram (Figure 1e) is reliable, and the close LUMO energy levels of the three materials (MAPbl₃, PCBM, and QAPDI) is more conducive

to electron injection and transport. Then, the thickness of the QAPDI interlayer can be varied from 0 to 15 nm to determine the influence of the thickness of the cathode interlayer on the device performance (see Figure S8) and the results are summarized in Table S2. With increasing thickness of the QAPDI layer from 0 nm to 5 nm, the device efficiencies of PSCs are improved from 16.81% to 20.51% due to the efficient electron injection and transport. However, with the increasing film thicknesses from 5 nm to 15 nm, the PCE values of PSCs are decreased partly because of the poor film morphology when the film thicknesses are increased. Figure 2a and Table 1 present the champion J-V curves for the control and QAPDI-based devices and the optimal device parameters, respectively. The devices with Bphen display the lower power conversion efficiencies (PCE) than those of QAPDI-based devices partly due to the mismatched LUMO energy levels between PCBM and Bphen. The LUMO level of Bphen is located at -3.00 eV, which is larger than the conduction band of MAPbl₃ and the LUMO level of PCBM, resulting in poor electron injection and transport. The best PCE of Bphen-based inverted PSCs is found to be 18.6% with a J_{sc} of 22.59 mA cm⁻², a V_{oc} of 1.114 V, and a FF of 0.7393, respectively. After using QAPDI as the cathode interlayer, all key J-V parameters were improved, affording the enhanced PCE of 20.55% along with a higher J_{sc} of 23.87 mA cm⁻², a V_{oc} of 1.130 V, and a FF of 0.7618. This is one of the highest efficiency reported for perylene diimide-based

PSCs to date.³⁶⁻⁵² The PCE values of perylene diimide-based PSCs are summarized in Table S3. Figure S9 shows that compared with the previous works, the best PCE value was obtained in this work, which suggests that QAPDI as a cathode interlayer could efficiently enhance the electron transport and improve the interface contact. In addition, the high electron mobility of QAPDI contributes to the higher J_{sc} and FF owing to the efficient electron injection and transport. Especially, the high FF values of QAPDI-based devices are attributed to the reduced charge recombination and improved interface contact that arise from the dipolar interface. The V_{oc} values increase from 1.114 V to 1.130 V owing to the fewer energy losses thanks to the adjacent energy levels between PCBM and QAPDI. To further reveal the influence of interlayer on the hysteresis effect in inverted PSCs, the J-V curves were measured for the control device and QAPDI-modified device. As expected, the less hysteresis effect for the QAPDI-based device is attained compared with that of the control device partly due to the higher electron transport and improved interface contact. The hysteresis index (HI) was calculated according to the literature.53, 54 Consequently, the HI value of the QAPDI-based device is 0.0041, which is lower than that of the control device (0.016), suggesting that the QAPDI interlayer can suppress the hysteresis effect in the inverted device.



Fig. 1 (a) Solution and film absorption spectra of QAPDI; (b) cyclic voltammogram of QAPDI in dichloromethane solution; (c) chemical structure of QADPI; (d) corresponding *J-V* curves of the electron-only SCLC devices with various active layers; (e) device configuration of inverted PSCs; (f) energy levels of materials.

Moreover, Figure 2b shows the external quantum efficiency (*EQE*) and the integrated photocurrent density for the two PSCs. It is clear that a strong photo-response spectrum of the QAPDI-based device is obtained in contrast to that of the control device, which could be attributed to the more efficient electron injection and collection at the interface between QAPDI and metal electrode. The integrated J_{sc} values were obtained as 21.68 and 22.55 mA cm⁻² for the control and QAPDI-based devices, respectively, which is in good agreement with the *J-V* investigation. Then, the stable photocurrent density and *PCE* for the two PSCs were conducted at the maximum power point as depicted in Figure 2c. As a result, the stable

photocurrent density values are found to be 21.85 and 23.38 mA cm⁻² together with the corresponding the *PCE* values to be 18.08% and 20.17% for the control and QAPDI-based devices, respectively. This implies that QAPDI as the cathode interlayer could steadily enhance the photocurrent density as well as *PCE* in the device. The *PCE* statistical distribution histograms of 40 individual devices with various cathode interlayers are summarized in Figure 2d. The standard deviation values of the two devices are reasonable, suggesting that the two devices are repeatable and reproducible. It is apparent that the devices with QAPDI interlayer show a higher *PCE* average values of 20.15±0.31% in comparison with that of the

control device (18.17 \pm 0.32%), which is consistent with the *J-V* results. This excellent performance indicates that QAPDI could be employed as a cathode interlayer to elevate the device efficiency for the inverted PSCs.

In order to comprehend the origin of the enhancement of the QAPDI-based PSCs, the surface morphologies of the MAPbI₃ films were measured by atomic force microscopy (AFM) and scanning electron microscopy (SEM). As depicted in Figures 3a-3c, three AFM height images of MAPbI₃ films are shown, and the root-mean-square (RMS) roughness values are found to be 17.01, 5.03, and 4.98 nm for the bare MAPbI₃ film and that covered by PCBM/Bphen or PCBM/QAPDI, respectively. These results suggest that the QAPDI-coated film exhibits better coverage than the control film, and such smooth surface morphology can be obtained for achieving excellent interface contact. In addition, there are lots of QAPDI crystals on the surface of the QAPDI-modified film, which is helpful for efficient electron transport. Figures 3d-3f show that the AFM 3D images for three kinds of films exhibit seriously decreased the depth of grain

boundaries from bare MAPbI₃ film to the QAPDI-covered film. The use of QAPDI as a cathode interlayer could form a continuous film over the complete MAPbI₃/PCBM surface along with good surface morphology and grain boundary. This facilitates the better stability of the perovskite layer due to the suppression of moisture in intruding into the perovskite film. In other words, a uniform and smooth interlayer film could contribute to the improved device parameters, which agrees well with the J-V characterization. Additionally, SEM top-view images of pristine MAPbI3 and that coated by PCBM/Bphen or PCBM/QAPDI are shown in Figures 3g-3i. There are some pinholes on the surface of the bare MAPbI₃ film. In comparison, the PCBM/Bphen and PCBM/QAPDI-modified films exhibit large grain-size distributions along with the smooth and pinhole-free film morphologies. Overall, AFM and SEM investigations demonstrate that the use of QAPDI as a cathode interlayer is an efficient strategy for the improvement of the interface contact and film coverage.



Fig. 2 (a) *J-V* curves of two devices with different scanning directions; (b) corresponding *EQE* spectra and the integrated *J_{sc}* curves of two devices; (c) the stabilized *J_{sc}* and *PCE* traces for two devices; (d) the statistics of the *PCE* distribution for two devices.

To gain further insight into the effect of the QAPDI interlayer on the device performance, the charge recombination mechanism in PSCs was investigated by measuring the change of J_{sc} or V_{oc} versus light intensity (*P*). Figure 4a shows the traces based on the dependence of light intensity on J_{sc} together with their linear model fitted to the data. According to J_{sc} versus P^{α} , the scaling factors (α) were estimated to be 0.93 and 0.95 for the control and QAPDIbased devices, respectively, indicating that the QAPDI modification could reduce bimolecular recombination because of efficient electron injection and decreased charge recombination. Furthermore, the plots based on the V_{oc} versus light intensity are shown in Figure 4b. The trap-assisted recombination is related to the slope of V_{oc} versus $P^{.55}$ Figure 4b shows that the excellent dependence of V_{oc} on light intensity was displayed, and the slopes of the two devices were calculated to 1.38 kT q⁻¹ for the control device and 1.29 kT q⁻¹ for the QAPDI-based device, respectively. These results reveal that decreased trap-assisted recombination is attributed to the efficient electron transport and improved interface contact, which is helpful for reducing energy losses in the device and thus increasing V_{oc} and *PCE*.

In order to gain a deeper understanding of the interlayer engineering in the improvement of device efficiency, the stable

photoluminescence (PL) spectra were measured for MAPbl₃ film with various modifications as shown in Figure 4c. The PL quenching phenomenon occurred as perovskite films were modified, and the PL intensity of the modified films decreased compared with the bare perovskite film. What is more, the QAPDI-coated film suffers from a significantly quenching in comparison to those of the PCBM or PCBM/Bphen-covered films. This indicates that the use of the QAPDI interlayer could efficiently enhance the electron extraction from the MAPbI_3 film to the interlayer, which is in good accordance with the J-V characterizations. Moreover, the trap density and electron mobility of the control and QAPDI-based devices were measured by the SCLC method. The electron-only SCLC devices were fabricated with the structure of ITO/SnO₂/MAPbI₃/PCBM/ Bphen or QAPDI/AI, and the J-V traces and the corresponding linear model fitted to the data are depicted in Figure 4d. The Bphen-based device is used as the control device to study the influence of QAPDI modification on the enhancement of device performance. According to the literature report,^{56, 57} the J-V traces have three different regions (OHMIC, TFL, and SCLC regions) to estimate the trap density and electron mobility in the device. The calculation results are summarized in Table 2. As a result, the trap density of the QAPDI-based film was found to be 1.40×10¹⁵ cm⁻³ (with the

trap-filled limit voltage of 0.32 V), which is lower than that of the control film (1.81×10^{15} cm⁻³, 0.41 V). These results demonstrate that the trap-assisted recombination in the QAPDI-modified film is restricted owing to the efficient electron transport and reduced energy level barrier. Meanwhile, the electron mobilities were calculated to be 0.021 cm² V⁻¹ s⁻¹ for the control film and 0.031 cm² V⁻¹ s⁻¹ for the QAPDI-modified film, respectively, suggesting that higher electron transport should be responsible for the higher photocurrent density and device efficiency, which is in agreement with the above analysis. Therefore, QAPDI is an outstanding cathode interlayer for high-efficiency inverted PSCs.

Tab. 1 Optimal device parameters of the PSCs with different cathode interlayers.						
Cathode interlayer	Scan direction	J _{sc}	Voc	FF	PCE	
		[mA cm ⁻²]	[V]	[%]	[%]	
Bphen	forward scan	22.13	1.119	73.97	18.31	
Bphen	reverse scan	22.59	1.114	73.93	18.61	
QAPDI	forward scan	23.75	1.131	76.37	20.51	
QAPDI	reverse scan	23.87	1.130	76.18	20.55	



Fig. 3 AFM height images of bare MAPbl₃ (a) and that coated by PCBM/Bphen (b) or PCBM/QAPDI (c); corresponding AFM 3D images of bare MAPbl₃ (d) and that coated by PCBM/Bphen (e) or PCBM/QAPDI (f); SEM top-view images of bare MAPbl₃ (g) and that coated by PCBM/Bphen (h) or PCBM/QAPDI (i).

At last, the stability of the two PSCs was measured under the ambient atmosphere with humidity of around 25%, and the devices were stored in dark condition. Both devices were encapsulated to measure the change in device efficiency. As depicted in Figure S10, the device efficiency of the QAPDI-based device was maintained at about 70% of its initial value after storage for 150 hours, whereas the device efficiency of the control device degraded by 35% of its

initial value after being stored under the same conditions for the same period of time. This investigation indicates that the improvement of interface contact and film coverage is beneficial for increasing the device stability.⁵⁸⁻⁶⁰ To understand the change of three kinds of film surfaces, the water contact angles based on the MAPbl₃ film respectively coated by PCBM, PCBM/Bphen, or PCBM/QAPDI were carried out as depicted in Figure S11. After Bphen or QAPDI modification, the water contact angles sharply

decreased. However, the average value of the contact angle of the QAPDI-modified film was found to be 86°, which is higher than that of the control film (81°). The high hydrophobicity of the QAPDI interlayer could inhibit the moisture permeation into the MAPbI₃ film, resulting in better stability of the PSCs.

Tab. 2 Trap density and electron mobility of the devices with different cathode interlayers.

Cathode	V _{TFL}	N _{trap}	μ_{e}
interlayer	[V]	[cm-3]	[cm ² V ⁻¹ s ⁻¹]
Bphen	0.41	1.81 × 10 ¹⁵	0.021
QAPDI	0.32	1.40 × 10 ¹⁵	0.031



Fig. 4 (a) Corresponding J_{sc} versus light intensity traces for two devices (symbols) together with a linear model fitted to the data (solid lines); (b) corresponding V_{oc} versus light intensity traces for two devices (symbols) together with a linear model fitted to the data (solid lines); (c) steady-state PL spectra for MAPbl₃ films, naked and that coated by PCBM, PCBM/Bphen, or PCBM/QAPDI; (d) corresponding *J-V* curves of the electron-only two perovskite-based SCLC devices with various cathode interlayers.

3. Conclusions

In summary, a novel perylene diimide-based zwitterion, namely QAPDI, was designed and synthesized by three-step reactions with a high overall yield. Due to the guaternary ammonium salt and largely conjugated framework, QAPDI has some advantages such as outstanding solubility in almost all organic solvents, appropriate energy levels (LUMO level is -3.99 eV), and high electron mobility. The inverted PSCs with the QAPDI interlayer have been developed, and the best PCE value was found to be 20.55% together with improved key device parameters. This excellent device performance could be attributed to the efficient QAPDI-based interlayer engineering that includes enhanced interface contact, reduced energy losses, and potent electron injection-transport-collection. Furthermore, the QAPDI-modified devices exhibit better ambient stability in comparison with the control devices because of the hydrophobicity of QAPDI and good film coverage, thereby inhibiting the degradation of the MAPbI₃ film. The practical and relevant development of organic small-molecular zwitterion as the cathode

interlayer would expedite the advancement of stable and high-performance inverted PSCs.

Conflicts of interest

The authors declare no conflict of interest.

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