

Bending-stability Interfacial Layer as Dual Electron Transport Layer for Flexible Organic Photovoltaics

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Electronic Supplementary Information

Abstract The flexibility of organic photovoltaics (OPVs) has attracted worldwide attention in recent years. To realize the bending-stability of OPVs, it is necessary to put forward the bending-stability of interfacial layer. A novel bendable composite is explored and successfully applied as an electron transport layer (ETL) for fully-flexible OPVs. We incorporated poly(vinylpyrrolidone)(PVP) into conjugated electrolytes (CPE) to composite a bendable ETL for high-performance OPVs devices. Fortunately, the devices based on PVP-modified CPE exhibited better device performances and more excellent mechanical properties of bendability. The fullerene-free OPVs based on PM6:IT-4F with CPE@PVP as ETLs yield the best power conversion efficiency (PCE) of 13.42%. Moreover, a satisfying efficiency of 12.59% has been obtained for the fully-flexible OPVs. As far as we know, this is one of the highest PCE for fully-flexible OPV based PM6:IT-4F system. More importantly, the flexible OPVs devices can retain more than 80% of its initial efficiency after 5000 bending cycles. Furthermore, among various curvature radii, the mechanical properties of the device based on CPE@PVP are superior to those of the device based on bare CPE as ETL. These findings indicate that the functional flexibility of CPE as a cathode interfacial layer is an effective strategy to fabricate high-performance flexible devices in the near future.

Keywords Bending-stability of interfacial layer; Conjugated electrolytes; Fully-flexible OPVs; Electron transport layers

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INTRODUCTION

Organic photovoltaics (OPVs) have been investigated deeply and attached much attention as the third generation photovoltaic technology due to its large-area solution processability, mechanical flexibility, light-weight and low-cost.^[1–4] Till now, power conversion efficiencies (PCE) of the small-area devices have been improved over 18.2%.^[5,6] However, large-area, wearable and flexible OPVs technology has not been developed rapidly in recent years.^[7–9] The flexibility of OPVs devices has attracted worldwide attention in recent years. Particularly, individual wearable electronic components must be flexible, easy processing and low-cost.^[10,11] Besides those exploring novel flexible transparent conductive electrodes,^[9] researchers have noticed the mechanical flexibility of active layers.^[12] Actually, up to now, there are only few reports on the flexibility of the electron transport layers (ETLs).^[13] In order to realize the

fully-flexible OPVs, it is necessary to put forward the mechanical bendability of the interfacial layer.^[14] Recently, the stability of phase separation and flexibility of active layers for OPVs devices has been concerned.^[12,14,15] However, the interfacial layer in OPV devices, which provides excitons extraction and charge transfer in the interlayer between the active layer and electrodes, is rarely reported.^[16] In fact, solution-processability, mechanical bendability and large-area manufacture technique of interlayer should all be taken into account.^[17] The selection of interfacial layer material mainly depends on its energy level and charge transfer characteristics. Thus, the design and synthesis of bendable interfacial layer materials for large-scale flexible organic solar cells device are particularly important. Unfortunately, it is difficult for the widely-used cathode interfacial materials to obtain a desired bending-stability property. Alkali metal salts (such as ZnO, LiF, CsF, Cs₂CO₃, Li₂CO₃, etc.)^[18–20] are usually accompanied by high-temperature processing and high elastic modulus. Therefore, these kinds of materials are not suitable for large-scale and flexible manufacture. Moreover, the low work function (WF) of metal materials (such as Ca and Ba) also applied for electron transport layer.^[18] These metal materials are usually instability in air and high energy consumption evaporation process, which limits their application in large-scale and flexible

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fabrication. Organic electrolyte materials, due to solution-processing, printability and low elastic modulus, are the most promising interfacial materials for large-area flexible and printable manufacture in the future.^[17]

Conjugated polymeric electrolyte (CPE), composed of a polymeric π -conjugated main chain and polar ionic as side group, was regarded as one of the most efficient organic electrolyte materials. As a result, the CPE possesses unique properties, such as good alcohol-solubility, interface dipole and uniform film formation. Therefore, intersecting solvents can be used in the device fabrication.^[21] Moreover, there is a dipole effect between the CPE and electrode. The dipole effect can tune the WF of electrode to match the molecular energy level of acceptor,^[22–24] so as to down-shift the charge injection barrier and improve the efficiency of charge collection in the corresponding electrodes.^[25,26] In addition, the interfacial layer has also an impact on the vertical phase separation of components of donor and acceptor in blend film, which is conducive to charge carriers selective collection.^[27] Therefore, interfacial engineering has significantly influenced the device performances.^[28–31] As a result, CPE has been successfully applied to OPVs device with state-of-the-art organic solar cells device. Particularly, Cao *et al.* have reported a series of CPEs (such as PNDIT-F3N and PNDIT-F3N-Br), which are based

on naphthalene-diimide (NDI) conjugated main chain unit with polar groups in the side chain (such as amino and ammonium).^[32–34] The NDI-based π -conjugated main chains endow the conjugated copolymers with an excellent electron mobility, resulting in broad application to all-polymer solar cells, organic transistors, organic light emitting diode, battery and perovskite solar cell. Its excellence interfacial modification and unique optoelectronic properties, enabled the devices to exhibit promising efficiency.

In this work, we introduce poly(vinylpyrrolidone) (PVP) into CPE to produce bendable electron transport layers for high-performance OPV devices, in account of the commercially available inexpensive PVP, with characteristics of alcohol-solubility, excellent film-forming property and self-assembly.^[35] The devices based on PVP-modified CPE exhibited high device performances and excellent mechanical properties of bendability. The fullerene-free OPVs based on PM6:IT-4F with 2% PVP-modified CPE as ETL yield the best power conversion efficiency (PCE) of 13.42%. More interestingly, a high PCE of 12.59% has been obtained for the fully-flexible OPVs based on PM6:IT-4F. Moreover, the flexible OPVs devices can retain over 80% of its initial PCE after 5000 bending cycles and under various curvature radii of the normalized PCE of device. Obviously, the OPV device based on CPE@PVP as ETL is super-

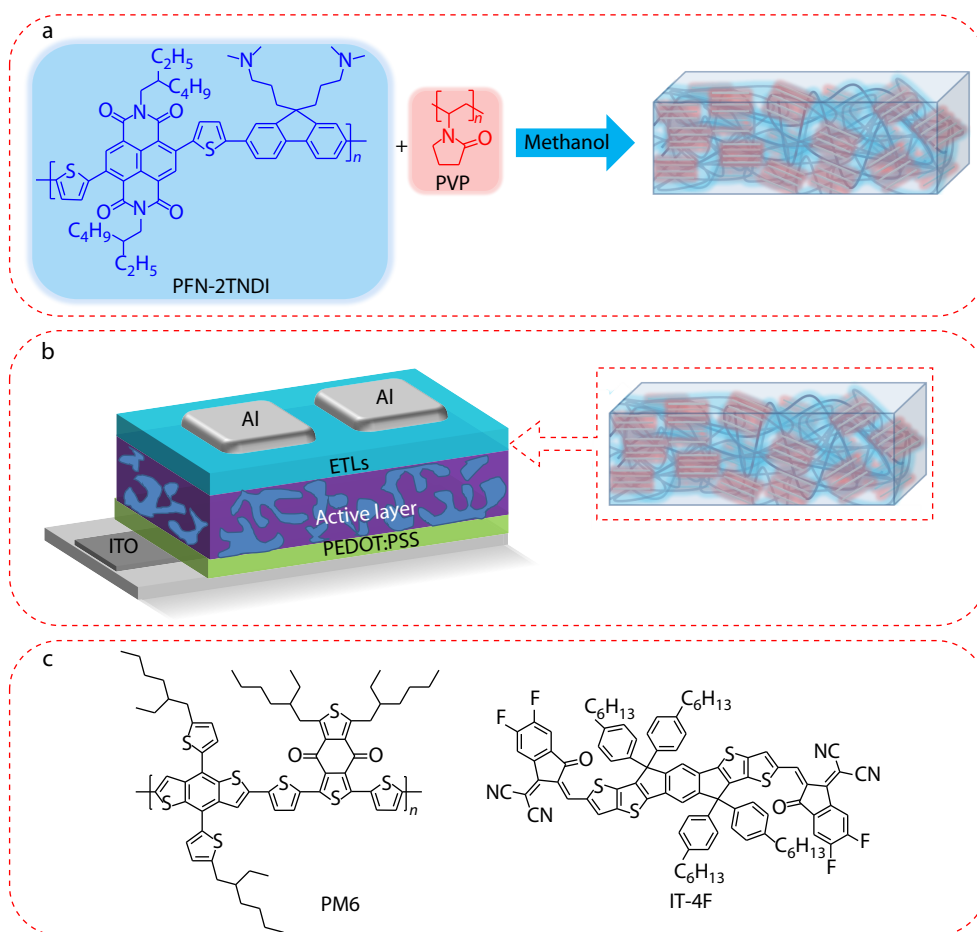


Fig. 1 (a) Schematic diagram of preparation of interfacial layer material; (b) The configuration of the fabricated conventional device; (c) The molecule structures of active layer materials.

ior to the bare device based on CPE as ETL. In addition, the PVP-modified CPE device showed a good universality for other active layer systems. Consequently, the best PCEs are 9.30% and 15.2% based on PTB7-Th:PC₇₁BM and PM6:Y6 system, respectively.

EXPERIMENTAL

Preparation of Bendable Interfacial Layer Materials

The processing of composite electron transport layer materials composite of interfacial layer materials is shown in Fig. 1(a). The conjugated polyelectrolyte (CPE) is poly[(9,9-bis(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene)-*alt*-5,5'-bis(2,2'-thiophene)-2,6-naphthalene-1,4,5,8-tetracarboxylic-*N,N'*-di(2-ethylhexyl)imide] (PNDI-F3N), and both CPE and poly(vinyl pyrrolidone) (PVP) can be easily dissolved in methanol. PNDI-F3N and PVP were mixed and dissolved in methanol in a certain proportion. The molecular weight of the PNDI-F3N, measured by gel permeation chromatography (GPC) using tetrahydrofuran as the eluent, was 13.0 kDa, and PVP with molecular weight of 2000 kDa was purchased from Alfar.

Device Fabrication

Device structure of ITO/PEDOT:PSS/PM6:IT-4F/ETLs/Al

A glass substrate with a pre-patterned ITO (sheet resistance = 15 $\Omega\cdot\text{sq}^{-1}$) was first ultrasonicated in acetone, detergent, deionized water and isopropanol in turn, and then modified by air plasma treatment for 3 min. After filtration through a 0.45 μm filter, PEDOT:PSS (Bay PVPAl4083, Bayer AG) was spin-coated at 4000 $\text{r}\cdot\text{min}^{-1}$ for 45 s to form a thin layer with a thickness of 40 nm on the cleaned ITO substrate, and baked on a hot plate at 140 $^{\circ}\text{C}$ for about 10 min. The PM6:IT-4F (1:1, *W/W*) was dissolved in chlorobenzene with 0.75 vol% 1,8-diiodooctane (DIO), mixed in solution with total concentration of 20 $\text{mg}\cdot\text{mL}^{-1}$, and spin-coated onto the interfacial layer at 2000 $\text{r}\cdot\text{min}^{-1}$ for 60 s. The PTB7-Th:PC₇₁BM (1:1.5, *W/W*) was dissolved in chlorobenzene with 3 vol% 1,8-diiodooctane (DIO), mixed in solution with total concentration of 25 $\text{mg}\cdot\text{mL}^{-1}$, and spin-coated onto the interfacial layer at 1000 $\text{r}\cdot\text{min}^{-1}$ for 2 min. The PM6:Y6 (1:1.2, *W/W*) was dissolved in chloroform with 0.5 vol% 1-chloronaphthalene (CN), mixed in solution with total concentration of 17.6 $\text{mg}\cdot\text{mL}^{-1}$, and spin-coated onto the interfacial layer at 3000 $\text{r}\cdot\text{min}^{-1}$ for 60 s. The cathode materials dissolved in methanol (1 $\text{mg}\cdot\text{mL}^{-1}$) was spin-coated on the active layer at 3000 $\text{r}\cdot\text{min}^{-1}$ for 60 s. Then the aluminum cathode was thermal evaporation over interface layer under a high vacuum chamber (7×10^{-4} Pa) to accomplish the device fabrication.

Device structure of PET/ITO/PEDOT:PSSPH1000/PM6:IT-4F/ETLs/Al

PET/ITO (sheet resistance = 15 $\Omega\cdot\text{sq}^{-1}$) was first ultrasonicated in acetone, detergent, deionized water and isopropanol in turn, and then modified by air plasma treatment for 3 min. After filtration through a 0.45 μm filter, PEDOT:PSS (PH1000) was blade-coating to get a thickness of 30 nm thin layer on the cleaned PET/ITO, and baked on a hot plate at 100 $^{\circ}\text{C}$ for about 10 min. The PM6:IT-4F (1:1, *W/W*) was dissolved in chlorobenzene with 0.75 vol% 1,8-diiodooctane (DIO), mixed in solution with total concentration of 20 $\text{mg}\cdot\text{mL}^{-1}$, spin-coated onto the interfacial layer at 2000 $\text{r}\cdot\text{min}^{-1}$ for 60 s, and then annealed at 100 $^{\circ}\text{C}$ for 10 min. The cathode materials dissolved in methanol

(1 $\text{mg}\cdot\text{mL}^{-1}$) was spin-coated on the active layer at 3000 $\text{r}\cdot\text{min}^{-1}$ for 60 s. Then the aluminum cathode was thermal evaporation over interface layer under a high vacuum chamber (7×10^{-4} Pa) to accomplish the device fabrication.

RESULTS AND DISCUSSION

In order to explore the effect of introduction various amounts of PVP into CPEs as ETL on the performance of OPVs devices, the conventional devices structure of ITO/PEDOT:PSS/PM6 (poly[1-(5-(4,8-bis(4-fluoro-5-(2-ethylhexyl) thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)thiophen-2-yl)-5,7-bis(2-ethylhexyl)-3-(thiophen-2-yl)-4*H*,8*H*-benzo[1,2-c:4,5-c']dithiophene-4,8-dione)):IT-4F(3,9-bis(5,6-difluoro-2-methylene-(3-(1,1-dicyanomethylene)-in-danone)-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-*d*:2',3'-*d'*]-s-indaceno[1,2-b:5,6-b']dithiophene)/ETLs/Ag was fabricated. The detailed information and preparation process of the devices have been provided in the electronic supplementary information (ESI). All ETLs were dissolved in methanol solution and spin-coating on the surface of active layer. The schematic diagram of the device structure is shown in Fig. 1(b). During this process, the bare CPE device was the controlled one. The composite interface layer was incorporating 1%, 2% and 5% PVP into the CPEs, respectively. The optimum *J*-*V* characteristic curve is presented in Fig. S1 (in ESI), and the corresponding device parameters are summarized in Table S1 (in ESI). The devices are based on various amounts of PVP incorporating CPE as ETLs, and the active layer is based on PM6:IT-4F to fabricate the devices. All the performances devices with various amounts of PVP modified CPE as ETLs are superior to the controlled device with bare CPE as ETL (PCE of 12.01%, with open-circuit voltage (V_{OC}) of 0.835 V, short-current density (J_{SC}) of 20.94 $\text{mA}\cdot\text{cm}^{-2}$, fill factor (FF) of 69.3%). As presented in Fig. 2(a) and Table 1, one of these ETLs, the 2% CPE@PVP shows the best PCE of 13.42%, with V_{OC} of 0.851 V, J_{SC} of 21.57 $\text{mA}\cdot\text{cm}^{-2}$ and FF of 73.1%. The corresponding external quantum efficiency (EQE) measurement can confirm the accuracy of J_{SC} . As shown in Fig. 2(b), the integral values calculated by the EQE and J_{SC} based on *J*-*V* characteristic curve are kept within the error range of 5%. Furthermore, the electron mobilities are measured by space charge limited current (SCLC) method with the electron-only devices (ITO/ZnO/PM6:IT-4F/ETLs/Al) (Fig. 2c) based on CPE and PVP modified CPE, and the electron mobilities are 1.21×10^{-3} and 1.33×10^{-3} $\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$, respectively. To investigate the difference of device carrier injection and collection based on CPE and CPE@PVP, the *J*-*V* characteristic curves of OPVs are measured under dark. As shown in Fig. 2(d), compared to CPE-based OPV, the CPE@PVP-based OPV is obviously suppressed on the side of the reverse current (from -2 V to 0 V). The suppressed dark current indicates that the less charges recombination, consequently contributes to the improvement of J_{SC} and FF.

In order to provide a deep insight into the improvement of the device performances, the electrode modified CPE and CPE@PVP are performed to estimate the work function (WF) of Al (cathode) by ultraviolet photoelectron spectroscopy (UPS) test (Figs. 3a and 3b). After deposition of CPE and CPE@PVP on the Al electrode, the WF showed a dramatic decrease. The lower WF can efficiently reduce Schottky barrier and form a suitable energy alignment between the active lay-

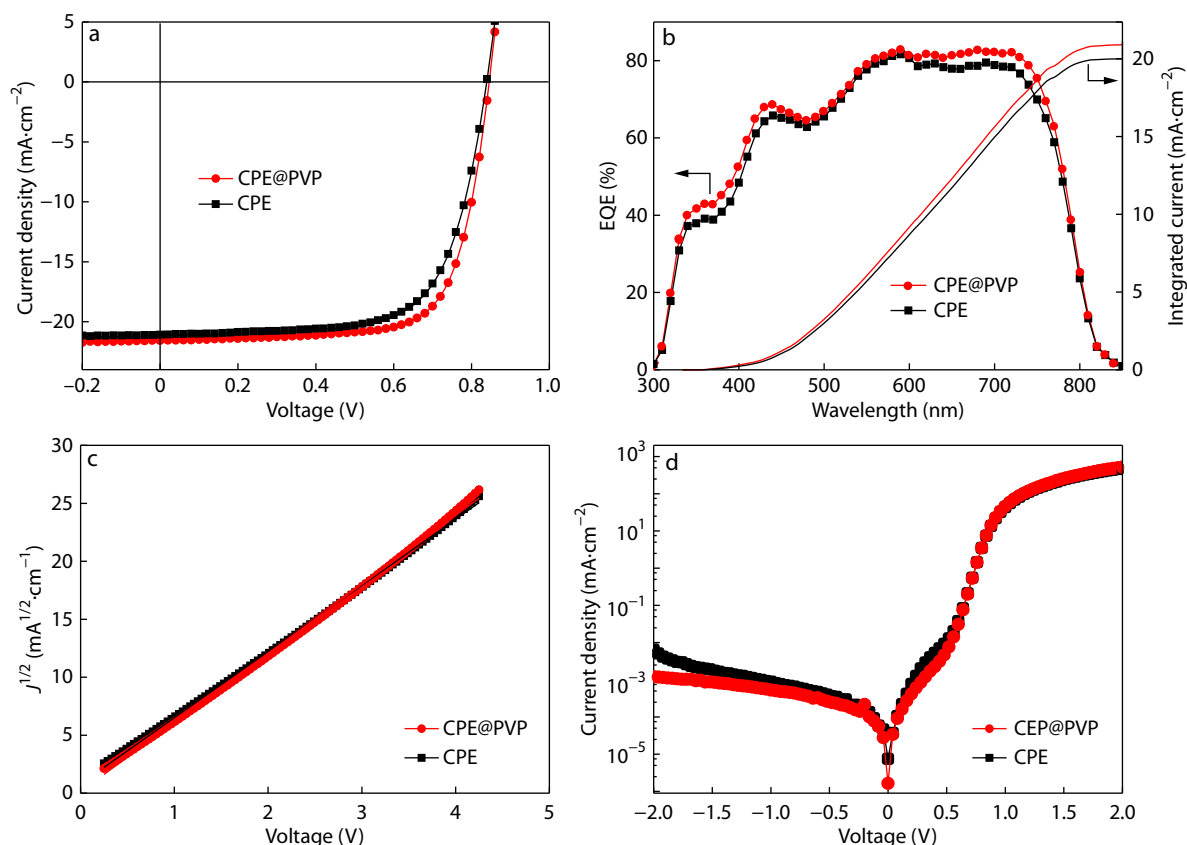


Fig. 2 (a) J - V curves of the OPVs devices ITO/PEDOT:PSS/PM6:IT-4F/ETLs/Al with various ETLs; (b) The corresponding EQE spectra of the PSCs based on PM6:IT-4F with various ETLs; (c) The corresponding $J^{1/2}$ - V characteristics of electron-only (ITO/ZnO/PM6:IT-4F/ETLs/Al) devices with various ETLs; (d) The corresponding dark current of device with various ETLs.

Table 1 Device parameters of inverted OPVs based on PM6:IT-4F active layer with CPE and CPE@PVP ETLs under AM 1.5 G irradiation (100 mA·cm⁻²). The normal device effective area is 0.04 cm² of a single chip and the flexible device effective area is 0.1 cm². The normal device structure is ITO/PEDOT:PSS/PM6:IT-4F/ETLs/Al and the flexible device structure is PET/PEDOT:PSS PH1000/PM6:IT-4F/ETLs/Al.

Device type	V_{OC} (V)	J_{SC} (mA·cm ⁻²)	FF (%)	PCE (%)
CPE	0.835±0.012	20.98±0.17 (19.85 ^c)	69.30±0.23	12.01 ^b (11.8 ^a ±0.23)
CPE@PVP	0.851±0.013	21.57±0.21 (20.75 ^c)	73.11±0.27	13.42 ^b (13.20 ^a ±0.22)
CPE-flexible OPV	0.860±0.010	16.09±0.19	73.84±0.19	10.22 ^b (9.95 ^a ±0.24)
CPE@PVP-flexible OPV	0.840±0.011	20.61±0.17	72.72±0.15	12.59 ^b (12.25 ^a ±0.30)

^a The averages for photovoltaic parameters of each device are given in parentheses with mean variation obtained from 10 devices, and the $\pm$ refer to the standard deviation; ^b Best device PCE; ^c Values are calculated from EQE.

er and cathode, consequently improving the electron injection. As for the CPE@PVP modified electrode, the WF showed further decrease. This phenomenon indicated that the amount of PVP incorporating into CPE had an impact on the decrease of its WF. As shown in Fig. 3, compared to the bare CPE/Al (WF=-3.75 eV), the calculated WF of CPE@PVP/Al was reduced to -3.70 eV. The modified Al with lower WF was helpful to alignment energy level between the cathode and acceptor, consequently improving the V_{OC} .

For the conventional device, the upper interfacial layer has little impact on the micromorphology of active layer. However, deposition of ETLs on active layer shows an impact on the contact between cathode and active layer. Fig. S2 and Table S2 (in ESI) show the water contact angle (θ) of interlayer deposited on the PM6:IT-4F blend film, the surface of pristine PM6:IT-4F is hydrophobic. After CPE deposited on the

surface of PM6:IT-4F blend film, the surface water contact angle decline to 86.1°, which means that the blend film became more hydrophilic. Replacing the CPE@PVP deposited on the top of PM6:IT-4F blend film, the contact angles decreased to 82.6°. The smaller contact angles mean that more polar groups are accumulated on the top surface of PM6:IT-4F blend film, which would improve the contact with the Al electrode. In addition, the PM6:IT-4F blend film with and without ETLs are measured by atomic force microscopy (AFM) to investigate the morphologies, as shown in Fig. S2 in ESI. Obviously, the pristine PM6:IT-4F blend film showed relatively rough surface with a root mean square (RMS) roughness of 6.08 nm. After deposited CPE and CPE@PVP on the active layer, the RMS decreased to 5.50 and 5.86 nm, respectively. The slightly improved RMS of blend film is conducive to intimate contact between the active layer and Al electrode, in favor of

the better device performances.

As is well-known, the intrinsic brittleness of interlayer limits its practical application in fully-flexible and wearable OPVs. To verify whether the effect of PVP incorporating into CPE can improve flexural endurance of ETL, the AFM peak-force model was performed to investigate the Young's modulus. As shown in Fig. 4(a), Young's modulus value of bare CPE film on glass is 510 MPa, which is higher than that of the CPE@PVP film on glass (346 MPa). This result means that less amount of PVP can significantly improve the mechanical bendability of ETL. After the introduction of PVP, due to its self-assembly and good compatibility with CPE, the aggregation of CPEs can be well dispersed, which is conducive to releasing the stress of the interface layer and obtaining better mechanical bending property. Furthermore, we tested the stress and strain curves bonded on polydimethylsiloxane (PDMS), the CPE@PVP shows more excellent mechanical properties. As shown in Fig. 4(b), the CPE@PVP bonded on PDMS exhibits lower stress under 10% strain curves, which means a better resilience used as the stability of bendability of ETLs for fully-flexible OPV. These results confirm that the incorporation of less PVP additives into CPE could improve mechanical bend-

ability of interface layer.

To evaluate the stability of CPE and CPE@PVP based fully-flexible device against external mechanical deformation, we performed the bending cycles test. The fully-flexible OPVs are fabricated with the device structure of PET/PEDOT:PSS(PH1000)/PM6:IT-4F/ETLs/Al, as shown in Fig. 5(a). The PCE based on CPE is 10.22% with a V_{OC} of 0.86 V, a J_{SC} of 16.09 $\text{mA}\cdot\text{cm}^{-2}$, an FF of 73.84%, and the efficiency based on CPE@PVP is 12.59%, with a V_{OC} of 0.84 V, a J_{SC} of 20.61 $\text{mA}\cdot\text{cm}^{-2}$, an FF of 70.72% (Fig. 5b). The normalized PCEs and under 5000 bending cycles with a radius of 1 cm of the corresponding device as a function are shown in Fig. 5(c). The CPE@PVP based fully-flexible device retains over 80% of its initial PCE. Furthermore, as shown in Fig. 5(d), various bending tests with curvature radius ranging from 0 mm to 1500 mm were carried out, and the CPE@PVP is superior to the bare CPE modified devices.

To investigate the universality of CETLs, the devices based on different active layer systems were exploited. The conventional device based on poly[[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-6-methyl]benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-

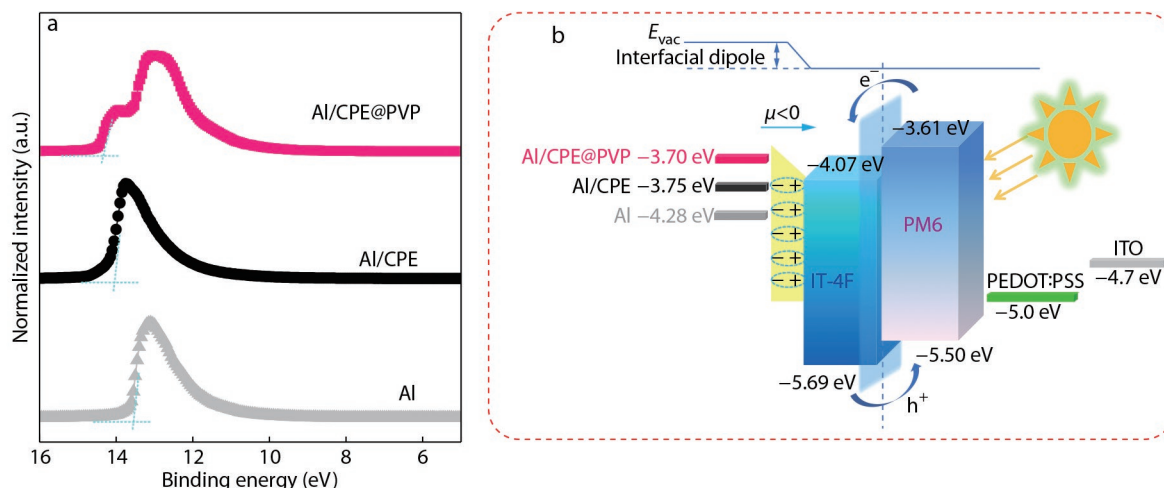


Fig. 3 (a) The ultraviolet photoelectron spectroscopy (UPS) of cathode modified by ETLs with or without of PVP; (b) Schematic diagram of donor and acceptor energy level structures and work functions.

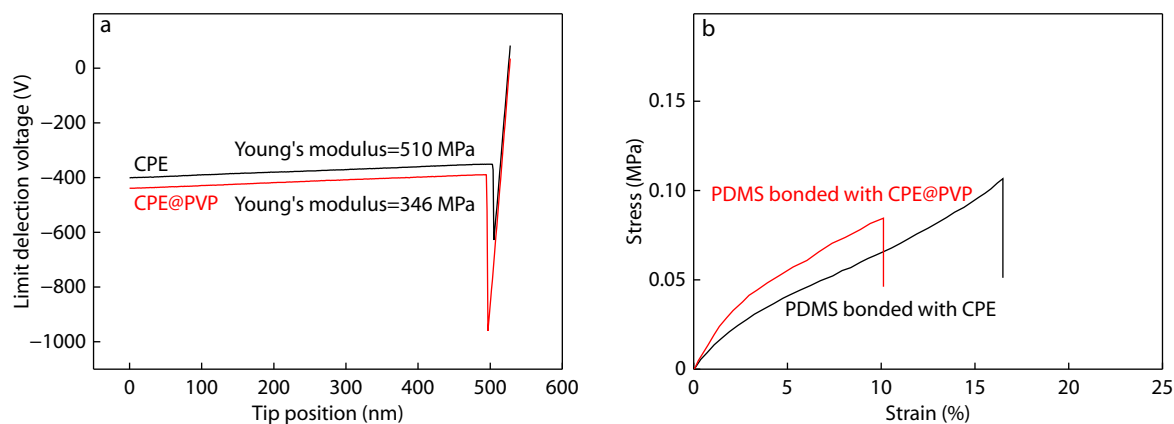


Fig. 4 (a) Young's modulus measured by peak-force model of atomic force microscopy (AFM) of with various ETLs on ITO; (b) Stress-strain curves of the PDMS bonded with CPE and CPE@PVP.

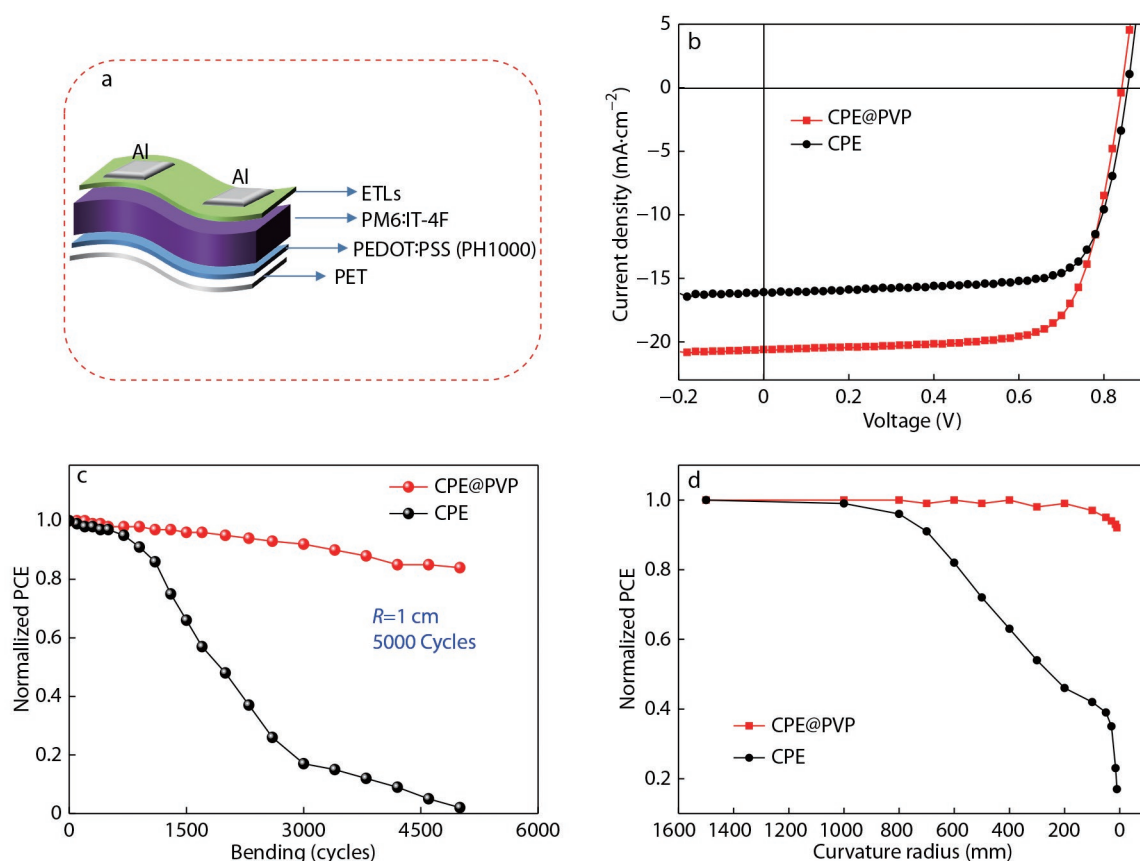


Fig. 5 (a) The configuration of the fully-flexible OPVs devices; (b) *J*-*V* curves of the fully-flexible OPVs devices PET/PEDOT: PSS(PH1000)/PM6:IT-4F/ETLs/Al with various ETLs; (c) The normalized PCE under various times bending cycles; (d) The normalized PCE under various curvature radii.

diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-*b*]thiophenediyl]] (PTB7-Th) as a donor and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) as an acceptor were fabricated. The corresponding *J*-*V* characteristics and device parameters are summarized in Fig. S3 and Table S2 in ESI. The ETL based on CPE@PVP as cathode interlayer yield an excellent PCE of 9.30%, higher than that of bare CPE (8.38%). And the increased PCEs of the CPE@PVP modified device are mainly related to the V_{OC} , J_{SC} and FF. Besides, we also applied the new composite interface layer in PM6:Y6 ((2,2'-((2Z,2'Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-*e*]thieno[2',3':4',5']thieno[2',3':4',5]pyrrolo[3,2-*g*]thieno[2',3':4',5]thieno[3,2-*b*]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalononitrile)) as active layer system with conventional device. A best PCE of 15.20% with a V_{OC} of 0.832 V, a J_{SC} of 25.10 mA·cm⁻², and an FF of 72.08% was achieved for the device based on CPE@PVP. Compared to the control devices, both of the CPE@PVP modified OPVs present enhanced device performances, mainly due to the improvement of V_{OC} , J_{SC} and FF values, which are consistent with the PM6:IT-4F-based device. These results indicated that the cathode interlayer *via* introduced by PVP into CPE exhibits a good universality for other high-performance active layer systems. Therefore, the CPE@PVP is a promising interfacial material for

large-area flexible and printable manufacture in the future.

CONCLUSIONS

In conclusion, we synthesized a bendable ETL by incorporating PVP into CPE and applying it to high-performance OPVs. The devices based on PVP-modified CPE exhibited higher efficiency and more excellent mechanical properties of bendability. As a result, the PVP-modified CPE obtained the best PCE of 13.42%, based on PM6:IT-4F. More importantly, an excellent PCE of 12.59% was obtained for the fully-flexible OPVs. As far as we know, this is one of the highest PCEs for fully-flexible OPV based PM6:IT-4F system. Furthermore, the fully-flexible OPV devices based on CPE@PVP can retain more than 80% of its initial PCE after 5000 bending cycles and the mechanical properties of device are superior to those of the barely CPE as ETLs under various curvature radii. These findings indicate that these composite interfacial materials are promising candidates as electron transport layer for flexible printable organic photovoltaic in the near future.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/>

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