

Planarized Polymer Acceptor Featuring High Electron Mobility for Efficient All-Polymer Solar Cells

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Electronic Supplementary Information

Abstract Significant progress has been achieved for all-polymer solar cells (APSCs) in the last few years by the use of polymerized small molecular acceptors (PSMAs). Developing high electron mobility polymer acceptors has been considered a feasible solution to further improve the photovoltaic performance of APSCs and fabricate thick film devices, which contributed to roll-to-roll printing techniques. In this work, we designed and synthesized PSV, an A-DA'D-A small molecule acceptor-based PSMA with the vinyl group as a bridged linkage to reduce the steric hindrance between the 1,1-dicyanomethylene-3-indanone (IC) terminal group. In comparison with the C—C bond linked polymer acceptor PS, PSV exhibits an almost planar conjugated framework and well-ordered molecular stacking in the thin film. Moreover, PSV exhibits superior n-type semiconducting properties with high electron mobility of up to $0.54 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is the highest value among reported PSMAs. By utilizing PM6 as a polymer donor, PSV-based blend forms a favorable nanomorphology and exhibits high and well-balanced hole/electron mobilities, which is beneficial for exciton separation and charge transport. Consequently, APSCs based on PM6:PSV achieved high power conversion efficiencies of up to 15.73%, with a simultaneously realized high V_{oc} of 0.923 V, J_{sc} of 23.2 mA cm^{-2} , and FF of 0.734. Such superior features enable PSV with excellent thickness-insensitive properties and over 13% PCE was obtained at 300 nm. To the best of our knowledge, the high PCE of 15.73% with excellent electron mobility of $0.54 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is the highest values reported for APSCs. These results point to the great significance of developing polymer acceptors with a high electron mobility for boosting the performance of APSCs.

Keywords All-polymer solar cells; Polymerized small molecular acceptors; Planarization; Electron mobility; Thick film organic solar cells

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INTRODUCTION

All-polymer solar cells (APSCs)^[1–7] have attracted increasing interest in the last two decades because of their potential advantages, such as good film-forming ability, outstanding mechanical durability, excellent photo- and thermal stability, and the easily tunable ink viscosity for large-scale fabrication.^[8–13] However, the power conversion efficiencies (PCEs) of APSCs are significantly lagging behind the small

molecular acceptors (SMAs).^[14–29] Considering the different interaction parameters between the polymer donors and polymer acceptors, the polymer blends tend to form large-sized phase separation, thereby deteriorating the charge separation and collection, leading to a low short-circuit current (J_{sc}) and fill factor (FF).^[30,31] Moreover, the rarity of efficient n-type building blocks^[32–36] mostly focused on the imide derivatives, also restricts the progress of APSCs. A landmark development of polymer acceptors was achieved in 2017, when Zhang *et al.*^[37] proposed the concept of polymerized small molecular acceptors (PSMAs) by copolymerizing SMAs as the main building block with a π -conjugated linkage. The PSMAs simultaneously inherited the merits of both SMAs (broad and strong light absorption and tunable energy levels) and polymers (good film-processing ability, flexibility, and morphological stability). Thus, a PCE of 9.19% was obtained for APSCs based on PZ1, the first PSMA, which had the highest

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PCE of the reported APSCs at that time. Recently, with the emergence of the A-DA'D-A-structured SMA Y6,^[38,39] APSCs based on the Y-series achieved a PCE of over 15%, benefiting from the broad and strong light absorption spectrum, well-formed nanomorphology, high electron mobility and low energy loss.^[40–54]

Despite the significant progress that has been achieved in PSMA, there is still much room to promote the PCEs of APSCs further. Developing polymer acceptors with high electron mobility is generally considered one of the most efficient pathways for constructing high-performance APSCs because of their dramatic effect on charge generation, recombination, and extraction.^[55–59] Generally, the conjugated polymer with shape-persistent or well-ordered backbone conformation is highly desired to increase the intermolecular charge transport because of the enhanced and ordered interchain π - π stacking. To date, the majority of PSMA using brominated 1,1-dicyanomethylene-3-indanone (IC-Br) as the terminal group, where two isomers exist, and the as-synthesized polymers contain three isomers, exhibiting a lower tendency to crystallize than their regioregular counterparts. Recently, two regioregular polymer acceptors independently reported by Luo *et al.*^[45] and Fu *et al.*,^[46] PY-IT and PZT- γ , presented enhanced crystallinity and higher mobility; thus, PCEs of over 15% were achieved, outperforming their regiorandom analogs. Another important issue needing thoughtful consideration is the backbone planarity of polymer acceptors.^[60] By reducing the steric hindrance, the resulting polymer acceptors would exhibit enlarged frontier molecular overlapping, enhanced intramolecular charge transfer with a lower bandgap, and a more ordered molecular packing with increased effective conjugation length, thereby resulting in efficient charge transport properties.^[61–65] However, the highest currently performing PSMA use thiophene derivatives as the linkage, yielding a relatively large twisting angle between the thiophene bridge and the IC terminals, which increases torsional disorder, thereby hampering the polymer interchain packing and lowering the resulting device performance.^[66]

The poly(*p*-phenylene vinylene) derivatives (PPVs), where vinyl is used as the bridge linkage between two phenyl units exhibiting good planarity, are one of the earliest and most comprehensively studied polymers in organic light-emitting diodes,^[67] organic photovoltaics,^[68] organic field-effect transistors (OFETs)^[69,70] and optically-pumped solid-state lasers.^[71,72] Inspired by the success of PPVs and combining it with the design rationale of improving the planarity of the conjugated backbone, in this work we introduced vinyl as the linkage moiety between the electron-withdrawing IC terminal units to synthesize the polymer acceptor PSV. In comparison to homopolymer PS, density functional theory (DFT) calculations revealed that the PSV polymer showed good planarity and well-ordered molecular stacking in thin films, and a high electron mobility of $0.54 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was revealed by OFET measurements. APSCs based on PM6:PSV gave a high PCE of up to 15.73%, with V_{oc} of 0.923 V, J_{sc} of 23.2 mA cm^{-2} , and FF of 0.734, which is much higher than that of the non-planar polymer PS with a moderate PCE of 10.29% because of the suppressed bimolecular recombination and efficient charge transport properties. These superior features endow PSV-based APSCs with excellent thickness-insensitive proper-

ties and over 13% PCE was obtained at 300 nm. To the best of our knowledge, the high PCE of 15.73% with excellent electron mobility of $0.54 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is the highest value reported for APSCs, which demonstrated that a planarized polymer acceptor with high electron mobility is a feasible solution for realizing high-efficiency APSCs.

EXPERIMENTAL

General Considerations

All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under inert atmosphere. Unless otherwise stated, starting materials were obtained from Adamas, Aldrich, and J&K and were used without any further purification. PM6 were purchased from Solarmer Material Inc. BTP-Br was synthesized according to the published procedures.^[39]

Synthesis of PS and PSV

Synthesis of PSV

BTP-Br (119 mg, 0.06 mmol) and *trans*-1,2-bis(tri-*n*-butylstannyl)ethylene (36.4 mg, 0.06 mmol) were dissolved in anhydrous toluene (3 mL) under nitrogen atmosphere, to which $\text{Pd}_2(\text{dba})_3$ (2.3 mg, 0.003 mmol) and $\text{P}(\text{o-tol})_3$ (1.8 mg, 0.06 mmol) were added. The reaction was stirred and refluxed for 12 h under dark. After cooling down to room temperature, the reaction mixture was poured into MeOH (50 mL) and then filtered. The residues were then subjected to Soxhlet extraction with methanol, hexane and chloroform successively. The resulting polymer was recovered as solid form the chloroform fraction by precipitation with methanol. The dark solid was dried under vacuum to give 63 mg of PSV in 57% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 9.30–9.10 (br, 1H), 8.95–8.35 (br, 3H), 8.18–7.30 (br, 5H), 5.12–4.58 (br, 3H), 3.44–2.91 (br, 3H), 2.40–2.06 (br, 2H), 2.04–1.73 (br, 2H), 1.73–0.36 (br, 74H). GPC: M_w =7.8 KDa; M_n =14.3 KDa; PDI=1.8.

Synthesis of PS

BTP-Br (119 mg, 0.06 mmol) and hexamethylditin (19.7 mg, 0.06 mmol) were dissolved in anhydrous toluene (2 mL) under nitrogen atmosphere, to which $\text{Pd}_2(\text{dba})_3$ (2.3 mg, 0.003 mmol) and $\text{P}(\text{o-tol})_3$ (1.8 mg, 0.06 mmol) were added. The reaction was stirred and refluxed for 72 h under dark. After cooling down to room temperature, the reaction mixture was poured into MeOH (50 mL) and then filtered. The residues were then subjected to Soxhlet extraction with methanol, hexane and chloroform successively. The resulting polymer was recovered as solid form the chloroform fraction by precipitation with methanol. The dark solid was dried under vacuum to give 39 mg of PS in 36% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 9.34–9.07 (br, 1H), 8.97–8.52 (br, 1H), 8.41–8.07 (br, 1H), 8.07–7.67 (br, 2H), 7.64–7.28 (br, 2H), 7.21–6.82 (br, 1H), 5.07–4.32 (br, 3H), 3.39–3.12 (br, 2H), 2.36–1.77 (br, 5H), 1.46–0.58 (br, 81H). GPC: M_w =7.3 KDa; M_n =11.1 KDa; PDI=1.5.

RESULTS AND DISCUSSION

Design, Synthesis and Optoelectronic Properties of PSMA

To get insight into the effects of the molecular configuration of polymerized small molecular acceptors (PSMA) on electronic

properties and photovoltaic performance, two PSMA, named as PSV and PS, were designed and synthesized with/without vinyl as the linkage moiety. As shown in Fig. 1(a), PSV was synthesized by the Stille coupling polycondensation of the regioregular monomer BTP-Br, obtained by Knoevenagel condensation of dialdehyde **1** with IC-Br, with *trans*-1,2-bis(tri-*n*-butylstannyl)ethylene using $\text{Pd}_2(\text{dba})_3/\text{P}(\text{o-tol})_3$ as the catalyst. The synthesis of the homopolymer PS was accomplished using hexamethylditin as the reactant, and the resulting polymer acceptor features C—C bond linked PSMA. Because of the introduction of long alkyl chains, both PSV and PS exhibit good solubility in common solvents, such as chloroform, chlorobenzene, and toluene. The number-/weight-average molecular weights (M_n , M_w) of PS and PSV are determined to be 7.3/11.1 kDa and 7.8/14.3 kDa, with a polydispersity index (M_w/M_n) of 1.5 and 1.8, respectively, which were measured by gel permeation chromatography. The target polymer PSV and PS showed good thermal stability characteristics with decomposition temperature (5% weight loss) of 344 and 300 °C, respectively, according to thermogravimetric analysis as shown in Fig. S1 (in the electronic supplementary information, ESI).

The optical properties of the polymer PSV and PS in dilute chloroform solution and solid film state were measured using the ultraviolet-visible (UV-Vis) absorption spectra as shown in

Fig. 1(b). Both the PSV and PS solution present broad and strong light absorption in the near-infrared region, while the maximum absorption peak of PSV at 760 nm is bathochromically shifted by 24 nm in comparison with PS, attributing to the extended π -conjugated backbone. The maximum absorption peaks of the PSV and PS thin film are located at 794 and 778 nm, with the absorption coefficients of $1.46 \times 10^5 \text{ cm}^{-1}$ and $0.92 \times 10^5 \text{ cm}^{-1}$, respectively (Fig. 1c). The absorption edges of PSV and PS pristine films are 883 and 876 nm, respectively, corresponding to the optical bandgaps of 1.40 and 1.42 eV, respectively. The extended π -conjugation backbone and increased absorption coefficient of PSV are beneficial for more sunlight-harvesting, and thus increases J_{sc} in APSCs. Cyclic voltammetry (CV) measurement was applied to check the electrochemical properties of PSV and PS (Fig. S2 in ESI), and the corresponding energy diagram is plotted in Fig. 1(d). Using the equation of $E_{\text{HOMO/LUMO}} = -(4.80 + E_{\text{ox/red}}^{\text{onset}}) \text{ eV}$, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of PSV and PS thin film were calculated to be $-5.63/-3.77 \text{ eV}$ and $-5.74/-3.79 \text{ eV}$, respectively, which matched well with polymer donor PM6,^[73] with a HOMO/LUMO energy level of $-5.50/-3.61 \text{ eV}$. To in-depth elucidate the effect of the linkage unit of PSMA on the molecular configuration and electronic properties,

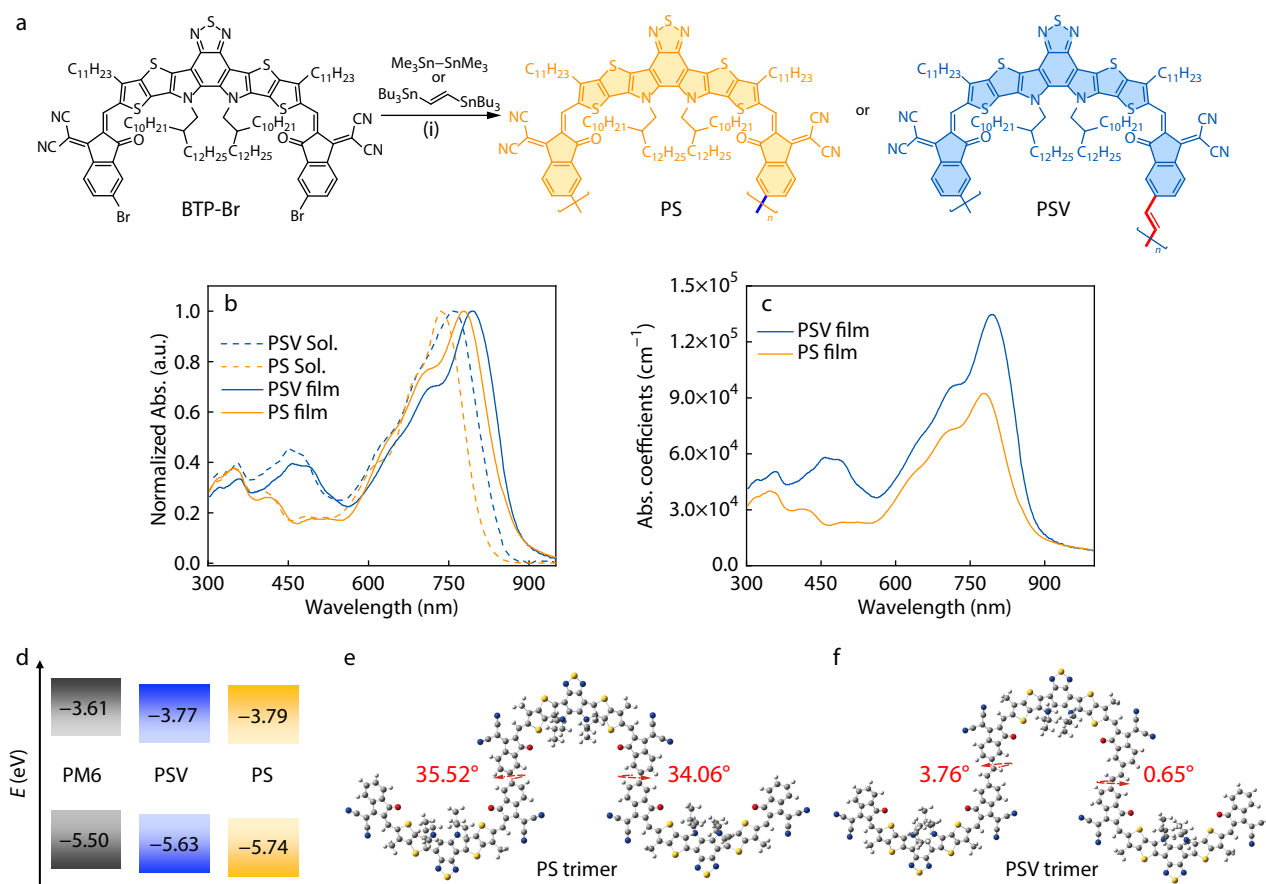


Fig. 1 (a) The synthetic routes of PS and PSV: (i) reaction conditions: $\text{Pd}_2(\text{dba})_3$, $\text{P}(\text{o-tol})_3$, toluene; (b) Normalized UV-Vis absorption spectra of PS and PSV in chloroform solution and solid films; (c) UV-Vis absorption spectra of PS and PSV thin films; (d) Schematic energy diagrams of PM6, PS and PSV films; Optimized geometry of PS trimer (e) and PSV trimer (f) obtained from density functional theory calculations using B3LYP/6-31G(d,p) basis.

density functional theory (DFT) calculations of PSV and PS oligomer analogs (three repeating units) were performed at the B3LPY/6-31G(d,p) basis set. As shown in Figs. 1(e) and 1(f), PSV trimer presents coplanar conjugated backbone; in particular, the dihedral angles between the adjacent IC terminal group are significantly reduced, ranging from 0.65° to 3.76° , in comparison with the PS trimer (34.06° – 35.52°). The planarized molecular backbone of PSV favors the LUMO electron densities overlapping with the adjacent IC terminal group, thus enhancing the intramolecular charge transfer in PSV than that of PS (Fig. S3 in ESI). Above all, PSV, in comparison with PS, with introducing the vinyl group into the molecular backbone exhibits a more planar molecular configuration, which would facilitate inter/intramolecular charge transfer, ordered π - π stacking, thus synergistically improving the charge transport properties.

The electron transport properties of PSV and PS thin films were well characterized using OFETs and space-charge limited current (SCLC) models. The fabrication details of OFET and SCLC devices are described in the Supporting Information. The transfer and output characteristics of the top-gate/bottom-contact (TG/BC) OFETs with a device structure of glass/Au/PSV/CYTOP/Al are presented in Figs. 2(a) and 2(b), and Fig. S4 (in ESI). Intriguingly, PSV thin film exhibits *n*-type transport characteristics with high electron mobility of $\mu_{\text{e,OFET}}=0.54 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is much higher than that of PS film with a value of $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. To the best of our knowledge, the high electron mobility of PSV is highest among ever reported PSMAs, which is comparable with the landmark polymer acceptor N2200.^[74] The SCLC electron transport properties of PSV and PS thin films were investigated utilizing the electron-only device structure composed of indium tin oxide (ITO)/ZnO/PSV or PS/PDINN (aliphatic amine-functionalized perylene-diimide)/Ag. The SCLC electron mo-

bilities ($\mu_{\text{e,SCLC}}$) are calculated to be $8.2\times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $2.99\times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for PSV and PS, respectively (Fig. 2c and Fig. S5 in ESI). Moreover, grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were performed to investigate the effect of molecular configuration on molecular packing and crystallinity in solid state, and even macroscopic electron mobility. The two-dimensional patterns and the corresponding line scattering profiles of PS and PSV thin films are illustrated in Figs. 2(d)–2(f). The neat film of PSV exhibits a semicrystalline structure with a favorable face-on orientation as indicated by the distinct (010) diffraction peak at $1.606 \text{ \AA}^{-1}$ in the out-of-plane (OOP) direction. The calculated π - π stacking distance is $3.91 \text{ \AA}$, with a coherence length (CCL) of 2.46 nm according to the Scherrer equation. The lamellar diffraction peak of PSV is located at $0.377 \text{ \AA}^{-1}$ in the IP direction, and the corresponding $d_{(100)}$ -spacing and CCL values are $16.69 \text{ \AA}$ and 3.63 nm , respectively. However, the PS pristine film shows relatively weak diffraction in alkyl chain and π - π stacking region, indicating the low crystallinity in film state. These results revealed that the molecular conformation strongly affects the intermolecular packing in the solid state, thus determining the interchain charge transport and even the device performance. The high electron mobility of PSV with well-ordered molecular stacking makes it an ideal polymer acceptor candidate for efficient all-polymer solar cells.

Photovoltaic Performance of APSCs

To evaluate the photovoltaic performance of new polymer acceptors, APSCs composed of a polymer acceptor (PSV or PS) and a PM6 donor possessing a complementary light absorption spectrum were fabricated with a conventional device structure of ITO/PEDOT:PSS/PM6:acceptor/PDINN/Ag. The optimized active blends were spin-coated from a chloroform solution (the APSCs fabrication details are described in ESI). The optimal *J*-*V* curves are plotted in Fig. 3(a), and the corresponding device

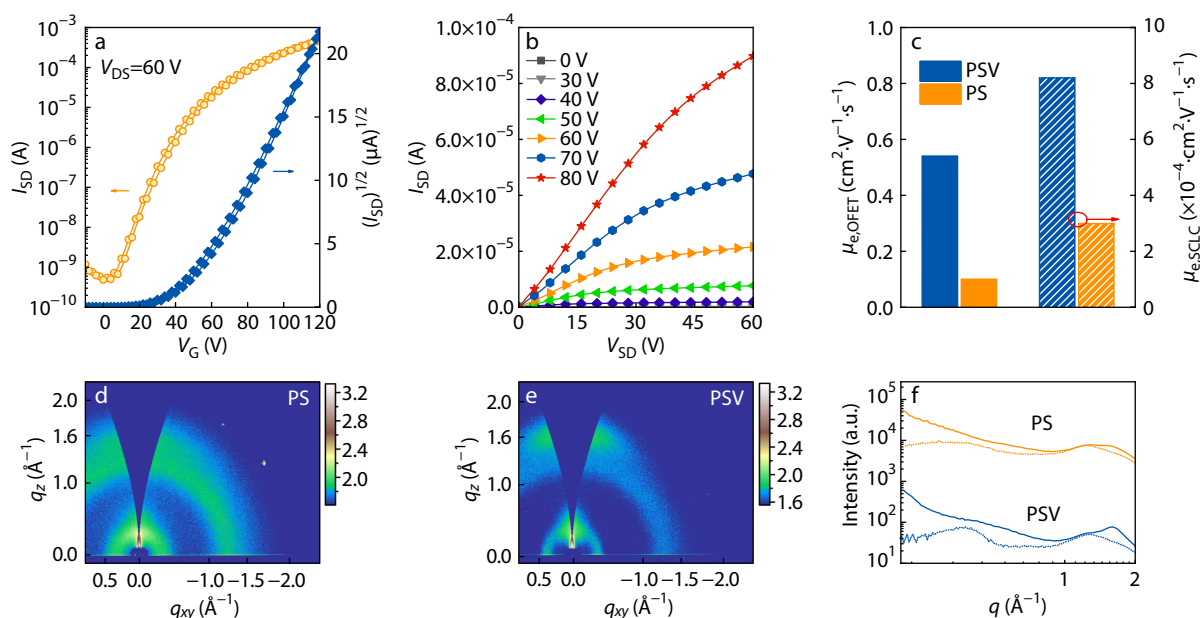


Fig. 2 The transfer characteristics (a) and output characteristics (b) of PSV thin film with a top-gate/bottom-contact organic field-effect transistor device structure. (c) The electron mobilities of PS and PSV measured by OFET and SCLC methods. Two-dimensional GIWAXS patterns of PS (d) and PSV (e) thin films. (f) IP (dotted line) and OOP (solid line) line cut profiles for PS and PSV thin films.

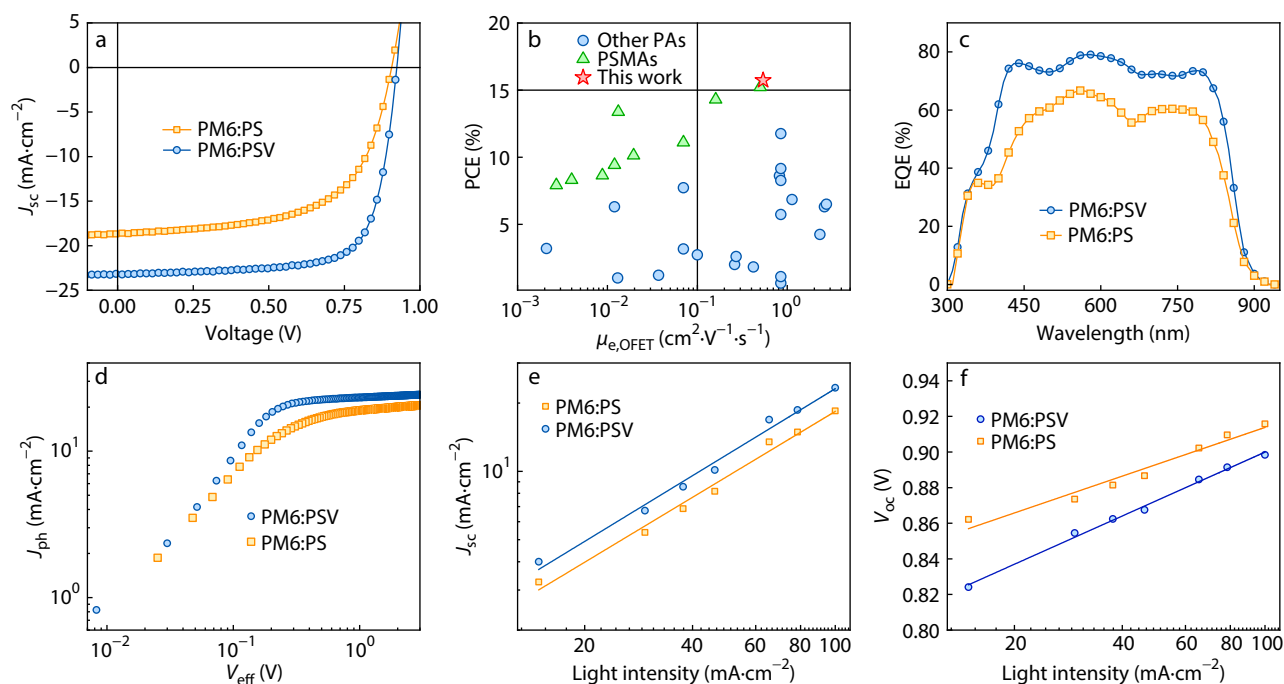


Fig. 3 (a) J - V curves of PS and PSV-based APSCs. (b) Reported statistics $\mu_{e,OFET}$ to PCE. (c) EQE characteristics of PS and PSV-based all-polymer solar cells. (d) J_{ph} - V_{eff} curves. (e) Light intensity dependence of J_{sc} . (f) Light intensity dependence of V_{oc} .

parameters are summarized in Table 1 and Table S1 (in ESI). The as-cast PM6:PSV blends deliver a PCE of 13.08%, with a V_{oc} of 0.931 V, J_{sc} of 21.9 $\text{mA}\cdot\text{cm}^{-2}$, and FF of 0.641. With the addition of solvent additive (1-chloronaphthalene) and thermal annealing treatment, the optimized PM6:PSV binary devices presented a champion PCE of 15.73%, with a simultaneously improved J_{sc} of 23.2 $\text{mA}\cdot\text{cm}^{-2}$, and FF of 0.734, which is among the best PCE with high electron mobility ever reported to date for APSCs (Fig. 3b). Moreover, the APSCs exhibited a low energy loss of 0.477 eV ($E_{loss} = E_g - V_{oc}$). On the contrary, the homopolymer acceptor PS-based APSCs deliver a relatively low PCE of 10.29%, with a V_{oc} of 0.906 V, J_{sc} of 18.7 $\text{mA}\cdot\text{cm}^{-2}$, and FF of 0.609. Moreover, the PM6:PSV-based APSCs exhibit superior reproducibility with an average PCE value of 15.51%, much higher than that of PM6:PS devices (PCE_{average} = 10.0%), which were obtained by statistical analysis of the corresponding 12 devices (Fig. S6 in ESI). The representative PSV-based APSCs simultaneously realized high V_{oc} , J_{sc} , and FF among the reported APSCs, thereby leading to high PCEs, which may ascribe to the high electron mobility of the polymer acceptor and the well-formed blend morphology, discussed as follows.

The corresponding external quantum efficiency (EQE) response spectra are shown in Fig. 3(c). Both the optimized PSV and PS-based devices exhibited broad EQE responses in the range of 300–880 nm, while the PM6:PSV blend exhibits much higher EQE values of over 70% in the range of 410–810 nm, which implies that the PSV acceptor can efficiently im-

prove the charge separation and transport properties in the binary system. The calculated J_{sc} values by integrating the corresponding EQE curves are 22.6 and 17.9 $\text{mA}\cdot\text{cm}^{-2}$ for PSV- and PS-based devices, respectively, which well-matched with the J_{sc} value obtained from the J - V curve.

Exciton Dissociation, Charge Recombination and Charge Transport Properties

In comparison to PM6:PS, PSV-based APSCs exhibit superior photovoltaic performance, especially in J_{sc} and FF, therefore, the charge generation, dissociation and recombination process is worth investigating in the blend films. The dependence of the photocurrent density (J_{ph}) on effective voltage (V_{eff}) was firstly measured to reveal the exciton dissociation and extraction processes in PSV- and PS-based APSCs. $J_{ph} = J_{light} - J_{dark}$, where J_{light} and J_{dark} denote as the current density under solar illumination and in the dark, respectively. $V_{eff} = V_0 - V_{app}$, where V_0 is the voltage when J_{ph} equals zero and V_{app} is the applied voltage. The J_{ph} value of PSV-based APSCs reaches a saturation current density (J_{sat}) close to 2 V, implying an efficient charge extraction (Fig. 3d). In contrast, the J_{ph} of PM6:PS blend cannot reach the saturation current even at a high V_{eff} , suggesting poor charge extraction. The calculated exciton dissociation probability $P(E,T)$ values, denoted as J_{ph}/J_{sat} , were 74%, 94%, and 98% for the PS and PSV-based devices under the maximum power output and short-circuit conditions, respectively. The charge recombination behavior of the APSCs was also investigated by the correlation between J_{sc} and light

Table 1 Photovoltaic performance of optimized APSCs based on PM6:PS and PM6:PSV under AM 1.5 G Illumination, 100 $\text{mW}\cdot\text{cm}^{-2}$.

Blends	V_{oc} (V)	J_{sc} ($\text{mA}\cdot\text{cm}^{-2}$)	J_{cal}^a ($\text{mA}\cdot\text{cm}^{-2}$)	FF (%)	PCE ^b (%)
PM6:PS	0.906	18.7	17.9	60.9	10.29 (10.0±0.26)
PM6:PSV	0.923	23.2	22.6	73.4	15.73 (15.51±0.15)

^a Integrated current density calculated from EQE spectra; ^b Average PCEs with standard deviation were obtained from 12 devices.

intensity (P_{light}), described by the formula of $J_{\text{sc}} \propto P_{\text{light}}^a$, where a is the exponential factor. If the value of a equals 1, it means that all the free charges in the device are swept out and efficiently collected by the electrode without bimolecular recombination. From Fig. 3(e), the calculated a values are 0.95 and 0.96 for the PM6:PS and PM6:PSV blends, respectively, indicating that the bimolecular recombination losses at short-circuit conditions were effectively minimized in PSV-based devices. We further fitted the dependences of V_{oc} and P_{light} using the equation of $V_{\text{oc}} \propto nkT/q \ln(P_{\text{light}})$, where k , T and q are the Boltzmann constant, the Kelvin temperature, and the elementary charge, respectively. If the slope of V_{oc} versus $\ln(P_{\text{light}})$ is close to $2kT/q$, it means that the dominant mechanism is monomolecular recombination; while the slope value equals kT/q suggesting the bimolecular recombination is the main pathway. The slope values were $1.52 kT/q$ and $1.16 kT/q$ for the PS and PSV-based devices, respectively (Fig. 3f), implying a significantly suppressed trap-assisted charge recombination in the optimized PM6:PSV blend. Overall, the efficient charge dissociation and mitigated bimolecular recombination are beneficial for achieving high J_{sc} and FF, leading to a high photovoltaic performance in the optimized PSV-based devices.

The charge-transporting properties of the blended films were investigated using the SCLC method (Fig. S7 in ESI). The electron and hole mobilities were measured using the device structure of ITO/ZnO/active layer/PDINN/Al and ITO/PEDOT:PSS/active layer/Au, respectively. For the PM6:PS thin film, the electron and hole mobilities were 1.3×10^{-4} and $3.9 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, with a μ_e/μ_h ratio of 0.33,

whereas the optimized blends exhibited higher electron and hole mobilities of 7.4×10^{-4} and $5.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, with a μ_e/μ_h ratio of 1.37. The higher and more balanced electron/hole mobilities were responsible for the high J_{sc} and FF in the optimized PSV-based APSCs, which also contributed to fabricate thickness-insensitive devices.

Transient Absorption Spectra Analysis

The photo-induced hole transfer dynamics in the PM6:PS and PM6:PSV blend films were also investigated by femtosecond time-resolved transient absorption (fs-TA) spectroscopy.^[75] Considering the donor and the acceptors show well-separated absorption peaks in the UV-Vis spectroscopy, the 800 nm laser was used as an excitation beam. We adjust the excitation power and keep the pump fluence less than 0.2 uJ cm^{-2} to guarantee only exciting the polymer acceptor, and reduce undesirable bimolecular processes. The singlet-singlet annihilation (SSA) can be ignored at our low excitation fluence. Figs. 4(a) and 4(b) show the color plot fs-TA spectra of the blend films and the fs-TA spectra at different time delays are displayed in Fig. S8 (in ESI). At the 800 nm pump, both PM6:PS and PM6:PSV thin films' fs-TA spectrum exhibit a ground state bleach (GSB) signal at $\approx 825 \text{ nm}$ which belongs to the acceptors. As the decay of polymer acceptors' bleaching signal, a clear GSB peak appears at the range of 550–650 nm, which is well-matched with the absorption spectrum of polymer donor PM6, implying an efficient hole transfer process occurred in the blends. The positive photo-induced absorption (PIA) signal at $\approx 900 \text{ nm}$ can be assigned as the polymer acceptors' local

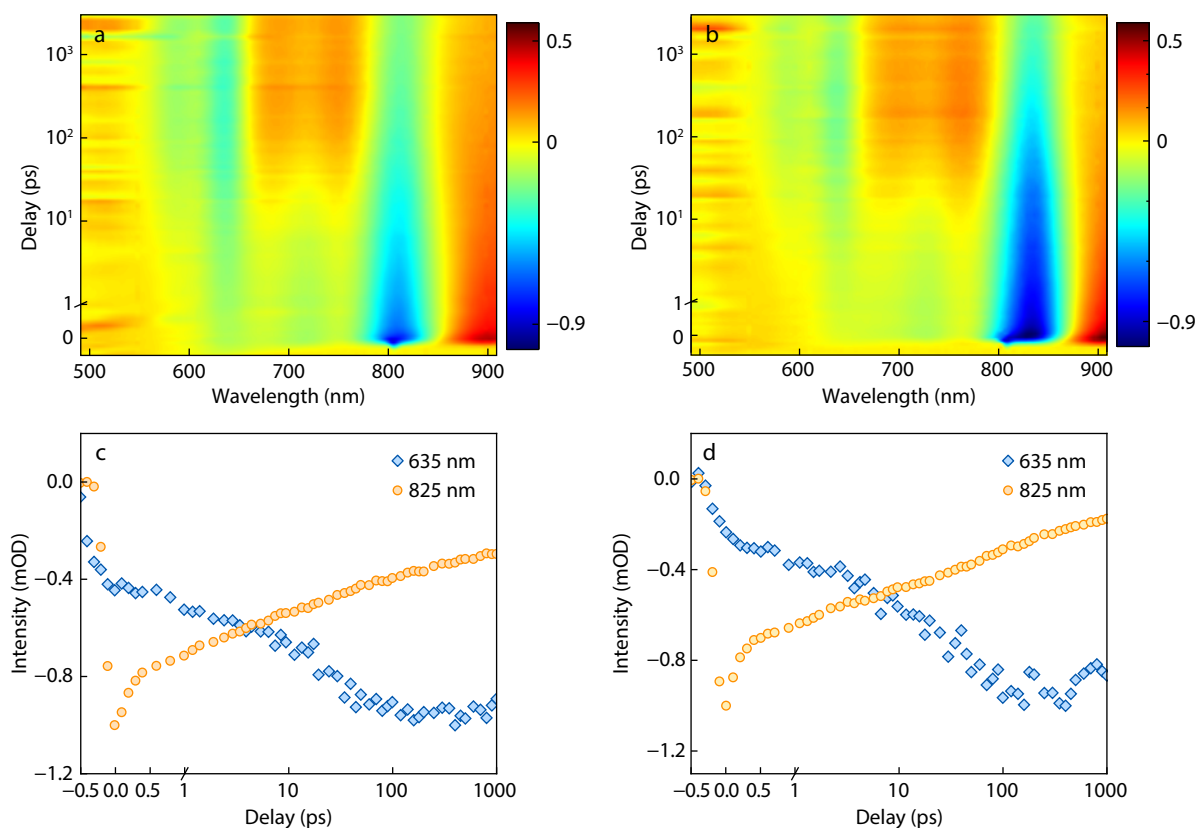


Fig. 4 (a, b) Femtosecond transient absorption spectra of PM6:PS and PM6:PSV blend films under 800 nm laser pumping; (c, d) Kinetic curves of PM6:PS and PM6:PSV blend films at 635 and 825 nm, respectively.

exciton absorption signal. Figs. 4(c) and 4(d) show the normalized dynamic plots at 635 and 825 nm in PM6:PS and PM6:PSV blends, respectively. To quantitatively analyze the hole transfer dynamics of the two blends, we fit the rising part of dynamics at 635 nm by a bi-exponential function. The time constants are $\tau_1=0.54\pm0.25$ ps, $\tau_2=24.34\pm4.37$ ps and $\tau_1=0.75\pm0.18$ ps, $\tau_2=30.47\pm4.92$ ps for the PM6:PSV and PM6:PS thin films, respectively, where τ_1 is assigned as the ultrafast exciton dissociation at the interface, and τ_2 is the exciton dissociation time in polymer acceptor domain. Compared to PM6:PS, PM6:PSV thin film exhibits a faster hole transfer process, which is consistent with the improved J_{sc} and FF, leading to superior device performance.

Morphology Analysis

Tapping-mode atomic force microscopy (AFM) was first applied to characterize the surface morphologies of the PSV:PM6 and PS:PM6 blend films. The PM6:PSV blend film showed a well-balanced phase separation and fibrous network morphology with a rougher surface, indicative of strong aggregation, as seen from the AFM images in comparison with the PM6:PS thin film (Figs. 5a and 5c and Fig. S9 in ESI). The surface root-mean-square roughness (R_q) of PM6:PSV blend film is 2.06 nm, whereas that of PM6:PS thin film is 1.30 nm. The larger surface roughness and enhanced fibrous aggregates indicated a more appropriate phase separation, which facilitated the charge dissociation and transfer, leading to the increase in J_{sc} and FF in PSV-based APSCs. The bulk morphology was further investigated by using transmission electron microscopy (TEM). From Figs. 5(b) and 5(d), PM6:PSV blend exhibits well-defined phase separation morphology, while PM6:PS blend film displays homogeneous morphology, which may ascribe to the low crystallinity of PS. Such kind of homogeneous morphology in PM6:PS film would hamper the charge transport to the electrode, leading to low J_{sc} and FF, which agrees well with the device performance.

To get insight into the photovoltaic performance differences in the APSCs, we further conducted grazing-incidence

wide-angle X-ray scattering to reveal the effect of molecular conformation on the crystallinity and molecular packing in the all-polymer mixture. The two-dimensional patterns and the corresponding line scattering profiles are shown in Figs. 5(e)–5(g) and Fig. S10 (in ESI). The PM6 pure film shows a dominant face-on orientation (Fig. S10 in ESI), with a (100) peak at $0.293\text{ \AA}^{-1}$ in the in-plane (IP) direction and a (010) peak at $1.647\text{ \AA}^{-1}$ in the out-of-plane (OOP) direction, corresponding to lamellar and π - π stacking distances of 21.41 and 3.82 Å, respectively. The crystal coherence lengths were calculated to be 5.8 and 2.1 nm. In Figs. 5(e) and 5(f), the blend films show combined structure profiles of both the polymer donor and the polymer acceptors. To better understand the evolution of blend morphology, peak-splitting fitting of the $0.2\text{--}0.5\text{ \AA}^{-1}$ region was performed by deconvoluting the (100) peaks into their donor and acceptor components. For the PM6:PS film, the CCLs of PM6 and PS were 4.07 and 2.96 nm, respectively. However, enhanced diffraction profiles from both (010) and (100) diffraction regions were observed in the PM6:PSV blend and the CCL₍₁₀₀₎s of PM6 and PSV were increased to 8.74 and 5.82 nm, respectively. Thus, the optimized PSV:PM6 film showed a much more favorable intermolecular packing and enhanced crystallinity, which is beneficial to improve the charge transport properties, and lead to high J_{sc} and FF values. Moreover, we also checked the shelf-stability of the APSCs without encapsulation in N_2 -filled glove box. As shown in Fig. S11 (in ESI), both PSV and PS-based devices presented good shelf-stability with low PCE losses after 6 days storage, benefiting from inherent morphology stability.

Thick Film of APSCs

Organic solar cells with thick photoactive layer are of great significance for industrial production by roll-to-roll manufacturing techniques. High charge carrier mobility is one of important parameters to meet the prerequisite for thickness-insensitive devices because of the efficient charge extraction

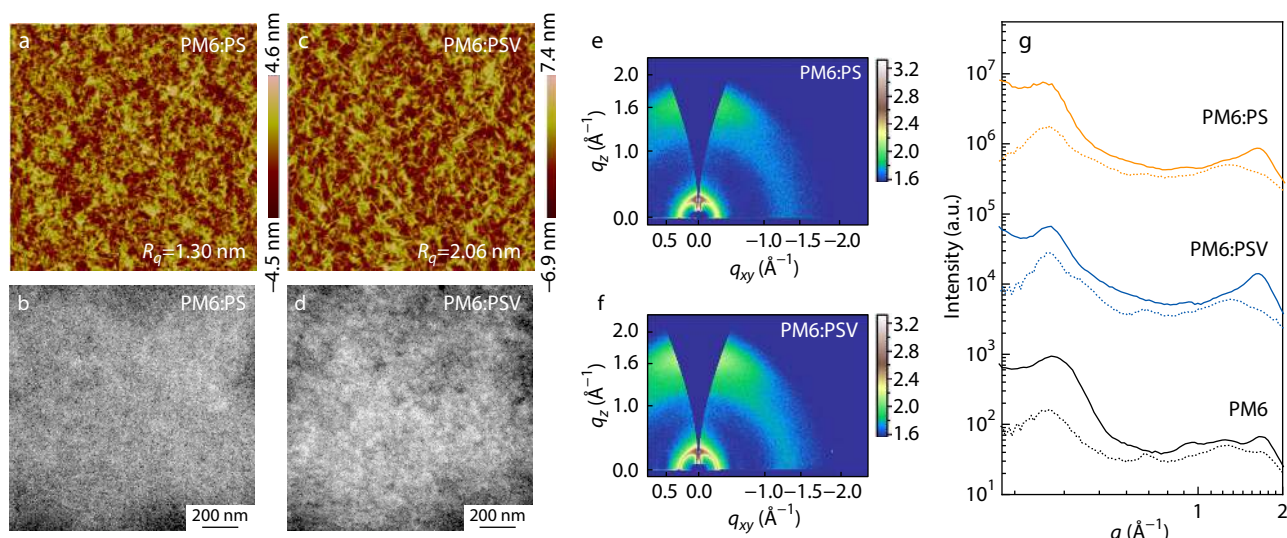


Fig. 5 Atomic force microscopy height images for PM6:PS (a) and PSV:PM6 (c) blend films. TEM images of PM6:PS (b) and PSV:PM6 (d) blends. Two-dimensional GIWAXS patterns of the PM6:PS (e) and PSV:PM6 (f) blends. (g) IP (dotted line) and OOP (solid line) line cut profiles for PM6, PM6:PS and PSV:PM6 thin films.

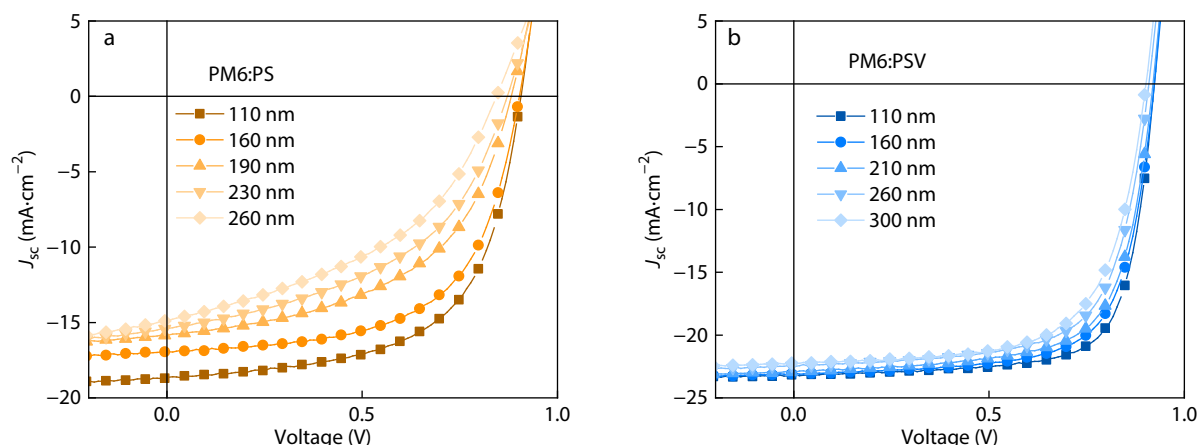


Fig. 6 *J-V* curves of PM6:PS (a) and PM6:PSV (b) blends with different film thickness.

and mitigated charge recombination. Herein, we conducted the dependence of the photovoltaic performance on blend film thickness and the corresponding *J-V* curves and photovoltaic parameters are presented in Fig. 6 and Table S2 (in ESI), respectively. Although both devices show a decline in the efficiency with the increasing of blend thickness, to our delight, PSV-based APSCs still achieved a high PCE of 13.3% even when the thickness reaches up to 300 nm, with a V_{oc} of 0.902 V, J_{sc} of 22.3 $\text{mA}\cdot\text{cm}^{-2}$, and FF of 0.663, maintaining 84.6% of the optimal efficiency. By contrast, PS-based APSCs is very sensitive to the thickness and only 53.5% of initial PCE was obtained as the thickness increased to 260 nm. As seen from Fig. 6(a) and Table S2 (in ESI), PS-based devices exhibit a relatively large drop of V_{oc} (from 0.906 V to 0.844 V) and FF (from 60.9% to 43.9%) with the increase of active layer thickness, which ascribed to the low and unbalanced hole/electron mobilities, thus inducing significant trap-assisted charge recombination in thicker blend films. The results are further demonstrated that planarized polymer acceptors with high electron mobility would be a potent way to obtain high-performance large-area printing APSCs device in the future.

CONCLUSIONS

In summary, we demonstrate the importance of the high electron mobility of polymer acceptors by planarizing the conjugated backbone to achieve high photovoltaic performance. In comparison with C—C bond linked polymer acceptor PS, PSV, an A-DA'D-A small molecule acceptor-based PSMA was designed and synthesized by using the vinyl group as the π -linkage to reduce the steric hindrance between the IC terminal group. PSV displayed a planarized molecular configuration and favorable intermolecular packing in the thin film. OFET devices based on PSV exhibit n-type semiconducting characteristics with high electron mobility of 0.54 $\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$. Moreover, PSV exhibited a near-infrared sunlight-harvesting spectrum with a large absorption coefficient and suitable energy levels. By matching PSV with PM6, a superior PCE of up to 15.73% was achieved, with a simultaneously realized high V_{oc} of 0.923 V, J_{sc} of 23.2 $\text{mA}\cdot\text{cm}^{-2}$, and FF of 0.734, which attributed to the formation of favorable bulk-heterojunction morphology and high and balanced electron/hole mobility, thus significantly

improve exciton dissociation and charge transport. To the best of our knowledge, the PCE value of 15.73% with superior electron mobility of 0.54 $\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ is among the highest values for APSCs. Additionally, APSCs based on PM6:PSV show excellent thickness-insensitive properties and a PCE of 13.3% was obtained at 300 nm. The results are inspiring for the further develop of polymer acceptor with high electron mobility and the boosting of the PCE of APSCs in the future.

NOTES

The authors declare no competing financial interest.



Electronic Supplementary Information

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