Contents lists available at ScienceDirect

Nano Energy

journal homepage: www.elsevier.com/locate/nanoen

Binary all-polymer solar cells with efficiency over 17% by fine-tuning halogenated thiophene linkers of polymer acceptors

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ARTICLE INFO

Keywords: Polymer acceptor Halogenated thiophene High-performance Flexible

ABSTRACT

All-polymer solar cells (APSCs) have achieved significant advances because of the rising of polymerized small molecular acceptors (PSMAs). While, the effect of halogen atoms on PSMAs in linkers has not been systematically studied. Herein, three PSMAs of PZC1, PZC2, and PZC3 are designed and synthesized by introducing fluorine and chlorine atom on the linkers to fine-tune their optoelectronic and molecular packing properties. Both halogenated polymer acceptors exhibit a slightly blue-shifted absorption range as well as deeper-lying frontier energy levels. When compared with non-halogenated PZC1, the fluorinated polymer acceptor (PZC2) presents better coplanar and rigid molecular conformation. The 3,4-dichlorothiophene-based polymer acceptor (PZC3) displays a distinctly twisted molecular chain between terminal groups and 3,4-dichlorothiophene owing to the steric hindrance between chlorine (Cl) and hydrogen (H) atoms. Due to the optimal morphologies in PM6:PZC2 film, the corresponding devices exhibit an excellent PCE of 17.30%, superior to those of PM6:PZC1 (13.83%) and PM6:PZC3 (15.75%) based devices. The mechanical robustness of three blend films is further investigated. PZC2-based films exhibit outstanding mechanical flexibility. Afterwards, the PM6:PZC2-based flexible devices achieve a PCE of 14.24%. Our results demonstrate that the usage of halogenated thiophene offers a practical way to fine-tune the performance of APSCs.

1. Introduction

All-polymer solar cells (APSC), composing of conjugated polymeric electron acceptor and electron donor materials, have drawn great attentions because of its great mechanical ductility and excellent morphological stability [1–5]. Before 2017, polymer acceptors featured with donor-acceptor (D-A) backbones mainly contain some electron-deficient units [6,7]. However, their shortcomings in absorption and charge mobility limit the performance of all-PSCs, which usually delivered unpleasant power conversion efficiencies (PCEs) below 12% [8,9]. Until 2017, a novel strategy that involves copolymerizing small-molecular acceptors (PSMAs) with π -bridge linkers were put

forward by Li group to synthesis polymer acceptors [10]. The PSMAs preserved some characters of small molecule acceptors (SMAs) and conjugated polymers, such as narrow bandgap, tunable energy levels, excellent mechanical properties, and higher stability [4]. Inspired by this strategy, numerous PSMAs were designed and reported. Recently, Y-series SMAs which exhibited excellent absorbance and small energy losses have attracted extensive attention. Afterwards, a lot of PSMAs based on Y-series SMAs have been reported, and the PCEs of all-PSC are closing to SMA-based PSCs [11–15].

It is noteworthy that π -bridge linkers are usually introduced to modify the characteristics of the corresponding PSMAs [16,17]. Currently, thiophene, 2,2'-bithiophene [9], and selenophene [18] are

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https://doi.org/10.1016/j.nanoen.2023.108766

Received 14 June 2023; Received in revised form 1 August 2023; Accepted 6 August 2023 Available online 7 August 2023 2211-2855/© 2023 Elsevier Ltd. All rights reserved.







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Fig. 1. (a) Chemical structures, and (b) Fragment of optimized trimers structures of PZC1, PZC2 and PZC3, respectively; (c) Normalized absorption spectra of PM6, PZC1, PZC2 and PZC3 in pristine films; (d) Variable-temperature absorption spectra of PZC1, PZC2 and PZC3 in chlorobenzene solution (e) Energy level diagrams of PM6, PZC1, PZC2 and PZC3.

usually adapted as the linkers in PSMAs. Considering the role of π -bridge, the molecular engineering of π -bridge linkers provides an alternative option to optimize properties of PSMAs. Besides, halogenation is thought to be a typical molecular innovation method to improve the performance of APSCs, including the PCEs and device stability [19, 20]. The underlying reasons could be attributed to the advantages of halogen atoms, such as their high electronegativity as well as small steric hindrance. Thus, their intrinsically characters (such as energy levels and absorption) could be well-adjusted by introducing different halogen atoms. Moreover, the enhanced intermolecular interactions, originated from the merits of halogen atoms, could strengthen intermolecular π - π stacking [21]. Min's works suggested that the optical properties, energy levels and molecular crystallinity of PSMAs can be well controlled via introducing halogens to the end group moiety [12,22]. However, the halogenation of end groups sometimes results in the regioisomeric issue which adversely affect the performance of all-PSCs [23–27]. Therefore, introducing halogens into π -bridge linkers of PSMAs may be an important and simple strategy to afford the efficient PSMAs.

With these in mind, considering the advantages of our newly developed CH series compounds [21,28–30], we developed three PSMAs (PZC1, PZC2 and PZC3) by polymerizing the CH series of SMAs unit with thiophene, 3,4-difluorothiophene and 3,4-dichlorothiophene to systematically tune their physicochemical and photovoltaic properties. Compared with PZC1 using thiophene linker, both PZC2 and PZC3

adopting halogenated thiophene linkers exhibit slightly blue-shift absorption range as well as deeper-lying energy levels. The 3,4-difluorothiophene-based polymer acceptor-PZC2 exhibits less twisting between the terminal groups and linkers, leading to a more co-planar molecular conformation. However, the 3,4-dichlorothiophene-based polymer-PZC3 displays more intramolecular twisting and less coplanarity. By combining with PM6, PZC1-based APSCs demonstrated a slightly low PCE of 13.83%. After introducing fluorine atom into linkers, PZC2-based APSCs afforded a high short-circuit current density (J_{sc}) of 24.61 mA cm⁻², contributing to its pleasant PCE of 17.30%. This thrilling result is linked to the efficient charge dynamics and restrained charge recombination, which are mainly determined by its suitable fiber-like phase separation with more ordered molecular packing. However, PZC3-based APSCs showed a moderate PCE of 15.75% with a $J_{\rm sc}$ of 22.34 mA cm^{-2} . This work highlights the facts that halogenated thiophene linkers could provide a feasible pathway to regulate the properties and thus the device performance of PSMAs.

2. Results and discussion

2.1. Material synthesis and calculations

Fig. 1a displays chemical structures of PZC1, PZC2 and PZC3, whose detailed synthetic procedures are shown in Scheme S1. Compound 1 was

Table 1

Optical property and energy levels of PZC1, PZC2 and PZC3.

Comp.	λ_{\max}^{sol} (nm)	$\lambda_{\max}^{\text{film}}$ (nm)	λ_{edge}^{film} (nm)	E ^{onset} (eV)	HOMO ^a (eV)	LUMO ^a (eV)	HOMO ^b (eV)	LUMO ^b (eV)
PZC1	788	801	861	1.44	-5.46	-3.56	-5.59	-3.72
PZC2	779	800	856	1.45	-5.48	-3.62	-5.62	-3.74
PZC3	758	799	852	1.46	-5.54	-3.65	-5.64	-3.75

^a Simulation results from DFT;

^b Experimental results from CV.



Fig. 2. (a) *J*-*V* curves, (b) PCE distributions, (c) EQE spectra, (d) *J*_{sc} vs. light intensity, (e) *J*_{ph}-*V*_{eff} curves, and (f) FTPS-EQEs of PM6:PZC1, PM6:PZC2 and PM6:PZC3-based APSCs, respectively.

obtained via our reported methods [28,31,32]. PZC1, PZC2 and PZC3 were obtained by copolymerizing compound 1 with different atom-substituted thiophene units, respectively. Decomposition temperatures of all polymer acceptors are over 330 °C as obtained from the thermogravimetric (TGA) measurements (Fig. S1), an indicator of their outstanding thermal stability. Density functional theory calculation method (B3LYP/6-31 G (d) basis set) was used to investigate the geometries of PZC1, PZC2 and PZC3 (Fig. S2). To illustrate the effect of halogen atoms on molecular geometries more clearly, the fragment of end group-linker-end group is displayed as Fig. 1b. The dihedral angle between the terminal group and the thiophene unit is about 23° in the case of PZC1, but the angle for PZC2 is reduced to nearly 10°. The small dihedral angle may lead to better coplanarity and conjugation of PZC2 which favors charge transporting. On the contrary, PZC3 shows a larger dihedral angle about 30°, originating from the large steric hindrance between Cl and H atoms [33,34].

2.2. Optical properties and energy levels

Fig. S3 show normalized absorption spectra of PZC1, PZC2 and PZC3 in dilute chloroform (CF) solutions, where display obvious absorption peaks of 788, 779 and 758 nm, respectively (Table 1), suggesting that the halogen atoms on linker will result in a blue-shift absorption. Besides, the degree of blue-shift for PZC3 are the most, which may be due

to more intramolecular twisting through 3,4-dichlorothiophene linkers [33–36]. However, all polymer acceptors exhibit quite similar absorption spectra in neat films, in which a similar absorption peak around 800 nm was observed for them (Fig. 1c and Table 1). In addition, the film absorption onsets (λ_{onset}) of PZC1, PZC2 and PZC3 are 861, 856 and 852 nm, respectively. Thus, their optical bandgaps are calculated to be 1.44, 1.45 and 1.46 eV, respectively. The variable-temperature absorption spectra of PZC1 to PZC3 in their chlorobenzene (CB) solutions were measured under the temperature from 20° to 100°C to investigate their aggregation properties (Fig. 1d). As results, the PZC2 show the most blue-shift vibrionic absorption peak (by 10 nm from 778 to 768 nm), an indicator of the stronger molecular packing in PZC2 [37]. Unlike PZC2, the absorption peaks of PZC3 are almost unchanged at elevated temperature which can be attributed to its twisted molecular chains [33,34].

The frontier orbital energy levels of three PSMAs were evaluated by electrochemical cyclic voltammetry (CV) and further estimated following the details in the Supporting Information (Fig. S4). As diagrammed in Fig. 1e, the frontier orbital energy levels of (LUMO/ HOMO) are -3.72/-5.59 eV for PZC1, -3.74/-5.62 eV for PZC2, and -3.75/-5.64 eV for PZC3, respectively. These results indicated that the halogenation on the linkers resulted in lowered energy levels of polymer acceptors, which may be caused by the electron-deficient property of halogenation [38,39]. The calculated energy levels of PZC1, PZC2 and PZC3 are depicted in Fig. S5, and the calculated

Table 2

Photovoltaic parameters of PZC1, PZC2, and PZC3 based APSCs. 15 independent top devices were used to calculate the average parameters listed in the parentheses.

Active layer	<i>V</i> _{oc} (V)	J _{sc} (mA cm ⁻²)	J ^{EQE} (mA cm ⁻²)	FF (%)	PCE (%)
PM6:	0.923	22.10	21.59	67.88	13.83
PZC1	(0.927	(22.21		(66.57	(13.68
	\pm 0.004)	\pm 0.12)		± 0.60)	\pm 0.08)
PM6:	0.936	24.61	24.15	74.93	17.30
PZC2	(0.936	(24.59		(74.34	(17.14
	\pm 0.003)	\pm 0.18)		± 0.36)	± 0.06)
PM6:	0.953	22.34	21.67	73.97	15.75
PZC3	(0.948	(22.38		(72.91	(15.46
	\pm 0.004)	± 0.09)		± 0.56)	\pm 0.13)

LUMO/HOMO levels follow the trends of experimental results.

2.3. Photovoltaic performance

To explore the device performance of PZC acceptors, conventional APSCs were fabricated and symmetrically studied. Their optimal current density-voltage (*J-V*) curves are shown in Fig. 2a, and the photovoltaic parameters are collected in Table 2. PZC1-based APSC showed a PCE of 13.83% with inferior J_{sc} and FF values, which are 22.10 mA cm⁻² and 67.88%. In comparison, PZC2-based APSCs achieved an enhanced J_{sc} of 24.61 mA cm⁻² together with a higher FF of 74.93%, and thus a champion PCE of 17.30%. With introducing chlorine atom, PZC3-based

devices exhibited a decreased J_{sc} and FF (22.34 mA cm⁻², 73.97%), resulting in a moderate PCE of 15.75%. The thermal stability of all-PSCs was studied under continuous heating of 60 °C in the glovebox filled with nitrogen. The PZC2-based APSC exhibited the best thermal stability with maintaining above 80% of its original performance after 280 h (Fig. S6), partially originating from its co-planar molecular conformation and the resultant stable morphologies [9].

As seen from their external quantum efficiency (EQE) spectra (Fig. 2c), all the devices show similar and broad photon response which is consistent with absorption range of the blended films (Fig. S3), while the PZC2-based devices exhibit an extended photon response to ~900 nm. Importantly, PZC2-based devices exhibit improved EQE from 300 to 900 nm, indicating higher photo-electron conversion efficiency, which contributes to the increased J_{sc} . Lastly, their integrated J_{sc} s are 21.59, 24.15, 21.67 mA cm⁻² for PZC1, PZC2 and PZC3-based devices, respectively, echoing their J_{sc} values in Table 1.

2.4. Charge dynamic investigation

The dependence of $J_{\rm sc}$ versus light intensity ($P_{\rm light}$), which follows the equation of $J_{\rm sc} \propto P_{\rm light}^{\alpha}$, was examined to reveal the bimolecular recombination [40]. As shown in Fig. 2d, the slope value α of PZC2 based device is closer to the unit, which is an indicator of the least bimolecular recombination occurred in PZC2-based APSCs. Fig. 2e presents the experimental results of the photogenerated current density ($J_{\rm ph}$) versus the effective voltage ($V_{\rm eff}$) in APSCs. Their exciton dissociation efficiencies, calculated by the value of $J_{\rm ph}/J_{\rm sat}$ under the short-circuit condition [41], are 95.47%, 97.01%, and 96.92% for PZC1, PZC2, and



Fig. 3. (a) AFM height images of APSCs; (b) GIWAXS patterns of PM6:PZC acceptors based blend films; (c) Line-cuts of the neat films and the blend films.



Fig. 4. (a) Optical micrographs of the formed cracks of PM6:PZC1, PM6:PZC2 and PM6:PZC3 blend films; (b) Histograms of Crack-onset Strain (COS) of PM6:PZC acceptors-based blend films; (c) *J-V* curve of PZC2-based flexible devices; (d) Normalized PCE value of the flexible devices with different bending cycles, and the radius of bending is set to 6 mm.

PZC3-based devices, respectively. Moreover, the charge collection efficiencies (η_{coll}), which are determined from J_{ph} under the maximum power output point divided by J_{sab} are 77.48%, 85.05%, and 83.77% for PZC1, PZC2, and PZC3-based devices, respectively. Thus, PZC2-based devices possess more efficient charge generation and collection process.

By conducting transient photocurrent (TPC) measurement, charge extraction time of PZC1, PZC2, and PZC3-based all-PSCs are calculated to be 0.31, 0.16 and 0.23 µs, respectively (Fig. S7a). Furthermore, the charge carrier lifetimes measured from transient photovoltage (TPV) measurement (Fig. S7b) are 15, 23, and 19 µs for PZC1, PZC2, and PZC3based APSCs, respectively. The fastest charge extraction time and prolonged carrier lifetime suggest the fact that the lowest charge recombination behaviors occur in PZC2-based devices [37,42]. The calculated electron mobility (μ_e) and hole mobility (μ_h) of PM6:PZC1 are 2.22×10^{-4} and 1.18×10^{-4} cm² V⁻¹ s⁻¹ (Fig. S8), respectively. Obviously improved charge transport behaviors with μ_e/μ_h of 5.89×10^{-4} $/4.46 \times 10^{-4}$ cm² V⁻¹ s⁻¹ are observed in PM6:PZC2 devices, explaining its high FF and J_{sc} values [43]. In comparison with those of PZC2 based devices, the μ_e/μ_h of PM6:PZC3 decrease to 2.94×10^{-4} /2.01 $\times 10^{-4}$ $\text{cm}^2 \text{ V}^1 \text{ s}^{-1}$, explaining why its FF and J_{sc} have decreased to a certain degree.

The energetic disorder has been considered as one of major loss mechanisms for the energy loss (E_{loss}) in devices [44], and the Urbach energy (E_U) is a measure of energetic disorder [44,45]. Fig. 2f reflects the Fourier-transform photocurrent spectroscopy EQE (FTPS-EQE) curves of all APSCs, which can be used to calculate the E_U values. As results, the smallest E_U of 22.9 meV is obtained for PZC2-based APSCs, enabling suppressed trap-assisted recombination of the charge. After all, PZC2-based APSC possess has the most efficient charge dynamics, and suppressed charge recombination, leading its best J_{sc} and FF.

2.5. Morphology analysis

The effect of halogenation on the morphological characteristics of blend films was revealed using atomic force microscopy (AFM) (Fig. 3a). PZC2-based blend film shows the smallest root mean square roughness (Rg) with a value of 1.13 nm, compared to that of PM6:PZC1 (1.22 nm) and PM6:PZC3 (1.50 nm), indicating that it has the smoothest surface [37,46]. Moreover, PM6:PZC2 blend film exhibits a more distinct bi-continuous network with uniform phase separation morphology in the phase image (Fig. S9), and these morpholgical features are thought to be beneifcal for charge separation and transport [47]. As contrast, PM6:PZC3 blend film shows the largest phase separation, which leads to the reduced D/A interfaces for exciton dissociation. The droplet contact angles were performed to stimate the Flory-Huggins interaction parameters χ (Fig. S10 and Table S1). The χ could be estimated by the equation of $\chi_{da} = K (\sqrt{\gamma_d} - \sqrt{\gamma_a})^2$, where *K* is a proportionality constant [37,38,48]. The calculated χ values are 0.248 K, 0.188 K, and 0.281 K for PM6:PZC1, PM6:PZC2, and PM6:PZC3 blend film, respectively. The smallest χ_{da} of PM6:PZC2 suggests the greatest miscibility leading to the most suitable phase separation.

Grazing incidence wide-angle X-ray scattering (GIWAXS) patterns and the corresponding line-cuts of the neat films are presented in Figs. S11 and 3c, respectively. As seen in Fig. S11, PZC acceptors preferred to adopt the face-on orientation, which can be supported by their obvious (100) diffraction peak in the in-plane (IP) direction and (010) diffraction peak in the out-of-plane (OOP) direction. All polymer acceptors exhibit similar (010) peak with π - π stacking distance (d_{π - π }) in the range of 4.01–4.08 Å (Table S2). The coherence lengths (CLs) of (010) orientation are calcualted to be 20.19 Å for PZC1, 21.10 Å for PZC2 and 18.54 Å for PZC3, respectively. The blending with PM6 did not change their face-on molecular orientions of PZC acceptors as evidenced by their GIWAXS profiles (Fig. 3b). The corresponding coherence lengths (CLs) of (010) orientation of blend films are 19.91 Å for PZC1, 21.92 Å for PZC2 and 21.50 Å for PZC3, respectively (Table S4). Overall, PZC2-based films display slightly larger (010) CLs than the other two PSMAs-based films, indicating the enhanced crystallinity with a coplanar molecular conformation.

2.6. Mechanical robustness

One of advantages of all-PSCs is their superior mechanical properties, and thus the mechanical robustness of the blend film was investigated by film-on elastomer (FOE) method [49–51]. The shape and propagation of cracks in three blend film is displayed in Fig. 4a, and the corresponding results are displayed in Fig. 4b. The crack onset strains (COSs) of three polymer-based blend film are 19.5%, 41.1% and 34.7%, respectively. The largest COS value of PZC2-based blend film indicates its excellent mechanical and flexible properties [11]. Subsequently, the flexible device was fabricated to deliver a PCE of 14.24%, whose J-Vcurve and EQE of flexible devices are shown in Figs. 4c and S12, respectively. It is exciting that after 1200 consecutive bending cycles (the bending radius is 6 mm), the PZC2-based flexible devices still maintain > 90% of its original performance (Fig. 4d), implying the decent mechanical stability of PZC2-based flexible devices.

3. Conclusion

To sum up, we developed a series of PSMAs constructed with halogenated or non-halogenated thiophene linkers. Both halogenated polymer acceptors (PZC2 and PZC3) exhibit a slightly blue-shift absorption range and deeper-lying energy levels owing to the electron-deficient properties of halogenation. Among them, PZC2 with fluorinated thiophene linker exhibits less twisting backbones and thus better intramolecular conjugation. On the contrary, the chlorinated polymer acceptors-PZC3 is twisted with a large dihedral angle of 37°. The PM6: PZC2-based blend film obtained a more obvious bi-continuous network and uniform phase separation morphological merits, contributing to the efficient charge dynamics along with suppressed charge recombination. As results, the pleasant $J_{\rm sc}$ (24.61 mA cm⁻²) and FF (74.93%) boost the performance of PZC2-based APSC with a best PCE of 17.30%, significantly higher than other two systems. This result represents one of very few PSMA with PCE over 17% of binary all-PSCs. Our work not only demonstrates that halogenation of linkers is a practical way to push up the performance of APSCs but also provides useful guidance for the selection of suitable halogen atoms.

CRediT authorship contribution statement

Zhe Zhang: Investigation, Visualization, Writing – original draft. Zhixiang Li: Investigation, Visualization. Bin Kan: Conceptualization, Supervision, Writing – review & editing. Tianqi Chen: Investigation. Yunxin Zhang: Investigation. Peiran Wang: Investigation. Zhaoyang Yao: Supervision, Writing – review & editing. Chenxi Li: Supervision. Bin Zhao: Investigation. Miaomiao Li: Investigation, Validation. Tainan Duan: Investigation, Validation. Xiangjian Wan: Supervision, Funding acquisition, Writing – review & editing. Yongsheng Chen: Conceptualization, Supervision, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

Acknowledgements

The authors gratefully acknowledge the financial support from MoST (2022YFB4200400, 2019YFA0705900) and NSFC (21935007, 52025033) of China, the 100 Young Academic Leaders Program of Nankai University (020-ZB22000110), the Fundamental Research Funds for the Central Universities, Nankai University (023-ZB22000105), and Haihe Laboratory of Sustainable Chemical Transformations. A portion of this work was based on the data obtained at BSRF-1W1A. The authors gratefully acknowledge the cooperation of the beamline scientists at BSRF-1W1A beamline.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2023.108766.

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