Contents lists available at ScienceDirect

Organic Electronics

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

Two nonlinear π -conjugated polymerized small molecular acceptors containing thiophene or 3,4-Difluorothiophene linkage unit for all-polymer solar cells

Zhe Zhang ^a, Hongbin Chen ^a, Zheng Xiao ^a, Yu Zhu ^a, Peiran Wang ^a, Yunxin Zhang ^b, Bin Kan ^{b,*}, Chenxi Li ^{a,**}, Yongsheng Chen ^a

^a State Key Laboratory and Institute of Elemento-Organic Chemistry, The Centre of Nanoscale Science and Technology and Key Laboratory of Functional Polymer Materials, Renewable Energy Conversion and Storage Center (RECAST), College of Chemistry, Nankai University, Tianjin, 300071, China ^b School of Materials Science and Engineering, Nankai University, Tianjin, 300071, China

ARTICLE INFO

Keywords: Polymer acceptor Nonlinear π-conjugated polymers All-polymer solar cells Fluorination Aggregation

ABSTRACT

Recently, lots of high-performance linear π -conjugated polymer acceptors based on the strategy of polymerizing small-molecule acceptors have been developed. However, there very few reports on nonlinear π -conjugated polymer acceptors for all-polymer solar cells. Here, we explored and synthesized two nonlinear π -conjugated polymer acceptors, named TZ1 or TZ2, respectively. Compared with the nonfluorinated polymer acceptor TZ1, the fluorinated polymer acceptor TZ2 presents lower energy level and better molecular aggregation. After blending with PM6, the TZ2-based device displayed more efficient exciton dissociation, higher charge carries mobilities and less charge recombination, leading to its higher J_{sc} of 14.94 mA cm⁻². As a result, the TZ2-based device achieved a PCE of 7.41%, higher than the TZ1-based device (4.06%). Our results provide a new strategy to develop nonlinear π -conjugated polymer acceptors and demonstrate the selection of suitable bridges is of importance for the construction of nonlinear π -conjugated polymer acceptors.

small molecule acceptor to solve these issues [20]. The resulting polymerized small molecule acceptors (PSMAs) not only preserve the ad-

vantages of small molecule acceptors (such as strong absorption

coefficient, good charge transport properties, small energy loss, etc. [19,

21]), but also preserve the advantages of polymers (such as thermal stability and mechanical flexibility) [19]. Inspired by this strategy and

the emerging high-performance Y6-based SMAs, the PCE of all-PSCs has

surpassed 17% recently [6,22]. At present, most of reported

high-performance polymer acceptors are linear π -conjugated polymers.

Compared with conventional linear π -conjugated polymers, nonlinear

 π -conjugated polymers featured 3D architectures (such as dendritic,

branched or star-shaped architecture) [23], are intrinsically stretched

and can contact with other polymers in multiple directions to tune the

interaction among different polymers [24]. Besides, nonlinear π -conju-

gated polymers tend to form globular structures which possess large

internal space that effectively inhibit the entanglement of adjacent

polymer chains through its large steric hindrance, consequently leads to

the enhanced solubility and miscibility with polymers [24-28]. Despite

1. Introduction

All-polymer solar cells (all-PSCs), which employ a π -conjugated polymer donor and a π -conjugated polymer acceptor, have attracted ever-increasing attention due to their advantages of excellent mechanical properties, good thermal stability, photostability and suitable for fabricating flexible device [1–5]. Despite the numerous advantages of all-PSCs, the power conversion efficiency (PCE) of all-PSCs [6] is still lagging behind the small-molecular acceptor based solar cells [7], which is mainly due to the limited kinds of high-performance polymer acceptors [8–13]. In early stage, various polymer acceptors based on naphthalene diimide [14], perylene diimide [15], diketopyrrolopyrrole [16], isoindigo [17], or B \leftarrow N bridge unit [18] have been explored. However, these polymer acceptors typically suffer from narrow absorption band, low extinction coefficient and unfavorable phase segregation [19]. As a result, most of these related all-PSCs presented moderate PCEs around 10% [19].

In 2017, Li et al. proposed an effective strategy by polymerizing

https://doi.org/10.1016/j.orgel.2022.106735

Received 30 September 2022; Received in revised form 14 November 2022; Accepted 27 December 2022 Available online 30 December 2022 1566-1199/© 2023 Elsevier B.V. All rights reserved.







^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: kanbin04@nankai.edu.cn (B. Kan), lichenxi@nankai.edu.cn (C. Li).

these characteristics, this architecture of polymer has been seldom employed as the polymer electron acceptor.

Herein, we propose a new strategy to synthesize nonlinear π -conjugated polymer acceptors by copolymerizing a small molecule acceptor with three reactive sites and a linkage unit with two reactive sites [24]. By using different linkage units, a variety of nonlinear π -conjugated polymer acceptors with easily tunable light absorption, energy level and aggregation behavior can be developed. Meanwhile, fluorination is widely adopted to improve the performance of all-PSCs, benefitting from the broaden absorption spectrum, the enhanced molecular aggregation and the favorable morphology of active layer [8,22,29,30]. With these in mind, the small molecule acceptor with three reactive sites was designed and synthesized according to our previous reports [29,31,32]. After then, thiophene and 3,4-difluoro thiophene were selected as the linkage unit to synthesize nonlinear π -conjugated polymer acceptors TZ1 and TZ2, respectively. The differences in their physicochemical and photovoltaic properties were systematically studied. Compared with TZ1, TZ2 shows a slightly red-shifted absorption and deeper-lying energy levels as well as stronger molecular aggregation. When blended with polymer donor PM6, both devices displayed considerable open-circuit voltages (V_{oc}) over 0.92 V. All-PSCs based on TZ2 demonstrated a PCE of 7.41%, with a short-circuit current density (J_{sc}) of 14.94 mA cm⁻², and a fill factor (FF) of 53.7%. While all-PSCs based on TZ1 suffered a quite low $J_{\rm sc}$ of 7.99 mA cm⁻², leading to its PCE of 4.06%. Our results provide an initial example to develop nonlinear π -conjugated polymer acceptors and demonstrate the selection of suitable bridges is also essential for the construction of nonlinear π -conjugated polymer acceptors.

2. Results and discussion

2.1. Materials and characterization

Molecular structures and synthetic routes of TZ1 and TZ2 are shown in Fig. 1, and the synthetic details were provided in the Supporting Information. The important intermediate compound **2** was prepared by converting compound **1** into a diimine by reduction and oxidation, then followed by an *in-situ* condensation with available 4-bromobenzene-1,2diamine. Then compound **3** was obtained from compound **2** through Vilsmeier-Haack reaction. Compound **4** was prepared by Konevenagel condensation of compound **3** with terminal group IC-Br. The chemical structures of all compounds were confirmed by nuclear magnetic resonance (NMR) spectra and mass spectra. Finally, the target polymer acceptors TZ1 and TZ2 were prepared via the typical Stille coupling reaction between compound **4** and thiophene unit, or difluoro-substituted thiophene unit, respectively. As measured by high temperature gel permeation chromatography (HT-GPC), the number-average molecular weights and polydispersity were 10.2 kDa/4.1 and 10.5 kDa/3.9. for TZ1 and TZ2, respectively. Both polymer acceptors show good solubility in common solvents, such as chloroform (CF) and chlorobenzene (CB), which is a prerequisite for fabricating the solution-processed devices.

2.2. Optical properties and energy levels

The UV–vis absorption spectra of TZ1 and TZ2 in diluted chloroform solution and neat film were measured. As shown in Fig. S1 (Supporting Information), TZ1 and TZ2 display similar absorption profiles in the solution. Compared with TZ1, the maximum absorption peak of TZ2 shows ~12 nm red-shifted (Table 1), which is caused by the enhanced intramolecular charge transfer (ICT) effect by the fluorine atoms [8,22, 30]. To investigate the aggregation behavior of these two polymer acceptors, variable-temperature UV–vis absorption spectra in cholrobenzene solution were measured in the range of 20–100 °C. As shown in Fig. 2a and b, TZ1 exhibits absorption range from 550 to 750 nm, and TZ2 exhibits more red-shifted absorption range from 600 to 800 nm. This result further confirms that the F atom can enhance intramolecular charge transfer (ICT) effect. More importantly, the TZ2 solution shows more red-shift vironic absorption peak (by 10 nm from 763 nm to 753

Table 1

Гŀ	ne o	ptical	and	electroc	hemical	data	of	TZ1	and	TZ2
----	------	--------	-----	----------	---------	------	----	-----	-----	-----

Comp.	λ_{\max}^{sol} (nm)	λ ^{film} (nm)	λ ^{film} (nm)	E ^{onset} (eV)	HOMO (eV)	LUMO (eV)
TZ1	756	797	852	1.46	-5.56	-3.72
TZ2	772	800	856	1.45	-5.57	-3.78



Fig. 1. (a) Molecular Structures of PM6 polymer donor, TZ1 and TZ2 polymer acceptors; (b) Synthetic route of TZ1 and TZ2 polymer acceptors.



Fig. 2. (a) Variable-temperature UV–vis absorption spectra of TZ1 in chlorobenzene; (b) Variable-temperature UV–vis absorption spectra of TZ2 in chlorobenzene; (c) Normalized absorption spectra of PM6, TZ1 and TZ2 in neat film; (d) Energy level diagrams of PM6, TZ1 and TZ2.

nm) than that of TZ1 solution (by 5 nm from 680 nm to 675 nm), which is an indicative of stronger molecular aggregation property of TZ2 [21]. In thin films, the maximum peaks of TZ1 and TZ2 are 797 nm and 800 nm, respectively. Compared with TZ2, TZ1 shows larger degree of red-shift from the solution state to the film state, implying that TZ1 exhibites quite different π - π stacking intercation and molecular aggreation between the solution and film state [33,34]. The absorption onsets of TZ1 and TZ2 film are 852 nm and 856 nm, respectively, which correspond to their similar optical bandgaps around 1.45 eV. As a result, the combination of polymer donor PM6 and these narrow bandgap polymer acceptors provides well complementary absorption extended to the near-infrared range (Fig. 2c) [21,34,35].

The froniter orbital energy levels of both polymer acceptors in films were meausred by cyclic voltammetry experiments under the identical and lowest unoccupied moleclar (LUMO) energy levels of TZ1 are estimated to be -5.56 eV and -3.72 eV, respectively. Due to the electronwithdrawing properties of F atom, TZ2 shows slightly down-shifted HOMO and LUMO energy levels, which are -5.57 eV and -3.78 eV, respectively. As illustrated in Fig. 2d, the energy levels of both polymer acceptors could match well with those of the polymer donor PM6. All above results demonstrate that the introduction of F-atom on the π -bridge of nonlinear π -conjugated polymer acceptors can tune their optical-electrical properties as well as the molecular aggregations.

conditions (Fig. S2). The highest occupied molecular orbital (HOMO)

2.3. Photovoltaic performance

To evaluate the photovoltaic potentials of these nonlinear



Fig. 3. (a) Device architecture of all-PSCs; (b) J-V curves of the all-PSCs; (c) EQE spectra of all-PSCs; (d) Hole and electron mobilities of PM6:TZ1 and PM6:TZ2 blends by SCLC measurement.

 π -conjugated polymer acceptors, all-polymer solar cells were fabricated with a conventional device architecture of ITO/PEDOT:PSS/PM6: PSMA/PNDIT-F3N/Ag (Fig. 3a), in which PM6 is selected as the electron donor material based on their matched energy levels and complementary absorptions. The concentration of PM6 was settled as 5 mg/mL, and the weight ratios of PM6:TZ1 and PM6:TZ2 were optimized to be 1:1.2. The thickness of both active layers was controlled to be 100 nm. The current density-voltage (*J-V*) curves of PM6:TZ1 and PM6:TZ2 were measured under simulated AM1.5G, 100 mW cm⁻². The details of the device fabrication and resulted photovoltaic parameters were shown in the Supporting Information.

As shown in Fig. 3b and Table 2, the devices based on PM6:TZ1 achieved a high V_{oc} of 0.932 V, but suffered an inferior J_{sc} of 7.99 mA cm⁻² and an FF of 54.6%, resulting in a low PCE of 4.06%. Though TZ2-based device had a similar V_{oc} of 0.925 V and an FF of 53.2%, the device offered an obvisouly higher PCE of 7.41%, which orginates from its almost twofold J_{sc} of 14.74 mA cm⁻² compared with that of TZ1-based device. The higher J_{sc} of TZ2-based device may be attributed to its slightly red-shifted absorption, more efficient exciton dissociation efficiency, faster charge transport, and less charge recombination as discussed below [36]. The results suggest that the introduction of F atoms into the backbone of the nonlinear π -conjugated polymers is an feasible method to enhance the performance.

To verify the realiability of $J_{\rm sc}$ values of all-PSC devices, external quantum efficiency (EQE) of the TZ1 and TZ2 based devices were measured and presented in Fig. 3c. Both devices show broad photoresponse from 300 to 900 nm. Compared with TZ1-based devices, TZ2-based devices display slightly red-shifted photoresponse which are consistent with their blend film absorptions. Meanwhile, TZ2-based devices show obviously higher EQE response from 300 to 900 nm, which agree well with the enhanced $J_{\rm sc}$. The integrated $J_{\rm sc}$ values from EQE curves are 7.87 mA cm⁻² and 14.25 mA cm⁻², respectively, which are well consistent with the $J_{\rm sc}$ values derived from their *J*-V curves.

2.4. Charge carrier generation, transporting and recombination

To investigate the effect of the F atoms of the linkage unit on exciton dissociation, steady-state photoluminescence (PL) of their blend films were measured (Fig. S3 and Fig. S4). The PL quenching efficiency of donor was calculated to be 79.6% in PM6:TZ1, and 82.1% in PM6:TZ2, respectively. However, the PL quenching efficiency of acceptor was only 10.3% in PM6:TZ1, and 53.5% in PM6:TZ2, respectively. Overall, the PL quenching efficiency of TZ2-based blended film is higher than that of TZ1, which indicates that the TZ2-based devices possess more efficient exciton dissociation [24]. This may be the reason why the EQE values of TZ2 is higher than that of TZ1 in the range of 700–900 nm. Even though TZ2 exhibits a higher quenching efficiency, the quenching efficiency of the acceptor moiety is lower than that of the donor moiety, suggesting the excitons generated in donor dissociate more easily than excitons generated in acceptors at the D/A interfaces. As shown in Fig. 2d, the LUMO energy offsets between PM6 and TZ1/TZ2 are both larger than their corrsponding HOMO energy offsets, which provide stronger driving force for separating the exciton generated in donor, supporting the above resutls [4,22,34,37].

To clarify the influence of F atoms on charge transport properties,

Table 2

Summary of photovoltaic parameters of all-PSCs, and the average parameters were calculated from 6 independent devices.

Active layer	$V_{\rm oc}$ (V)	J _{sc} (mA cm ⁻²)	J ^{cal} (mA cm ⁻²)	FF (%)	PCE (%)
PM6:	0.932 (0.935	7.99 (7.77	7.87	54.6 (54.6	4.06 (3.96
TZ1	\pm 0.002)	\pm 0.14)		\pm 0.3)	\pm 0.06)
PM6:	0.925 (0.921	14.94	14.25	53.7 (53.3	7.41 (7.33
TZ2	\pm 0.002)	(14.91 \pm		± 0.6)	\pm 0.07)
		0.11)			

hole (μ_h) and electron mobility (μ_e) of blend films were measured by space-charge-limited-current method (Fig. 3d and Fig. S5). The electron and hole mobilities of the PM6:TZ1 blended film are 3.13×10^{-6} cm² V^{-1} s⁻¹ and 7.38×10^{-5} cm² V^{-1} s⁻¹, respectively, which are both lower than those of the PM6:TZ2 blended film ($\mu_e = 6.16 \times 10^{-6}$ cm² V^{-1} s⁻¹). The PM6:TZ2 device not only has higher carrier mobility, but also has more balanced hole/electron mobility [38]. These results indicate the introduction of F atoms into the polymer backbone can improve the carrier mobilities, and thus the charge transport properties. While, the highly unbalanced hole/electron mobility may be one of the important reasons for their low FFs and PCEs.

The dependence of J_{sc} on the light intensity (P_{light}) was conducted to probe the bimolecular recombination behaviors in the devices. The relationship between J_{sc} and P_{light} could be expressed as a mathematical equation [39]: $J_{sc} \propto P_{light}^{\alpha}$. By fitting the date of J_{sc} and P_{light} (Fig. 4a), the α value of TZ2-based device is 0.99, which is larger than that of TZ1 based device ($\alpha = 0.95$), indicating that TZ2-based device possesses less bimolecular recombination. Besides, the dependence of Voc on light intensity (P_{light}) was meaured. The relationship between V_{oc} and P_{light} is expressed by the equation of $V_{\rm oc} \propto nkT/q \ln(P_{\rm light})$, where k is the Boltzmann constant, T is the Kelvin temperature, and g is the elementary charge [40]. When n is close to 1, bimolecuar recombination is domiant recombination mechanism. On the contrary, when n is close to 2, the main recombination mechanism is trap-assisted recombination. As shown in Fig. 4b, the n value of PM6:TZ1 and PM6:TZ2 devices are 1.12 and 1.26, respectively, indicating that PM6:TZ1 suffers less trap-assisted recombination.. Furthermore, transient potocurrent (TPC) and the transient photovoltage (TPV) were used to investigate the charge extraction and recombination process in both devices. As shown in Fig. 4c, the charge extraction times of PM6:TZ1 and PM6:TZ2 devices are 0.41 µs and 0.25 µs, respectively, indicating PM6:TZ2 devices has faster charge extration process. The charge carrier lifetime calculated from the TPV result is 92 μ s for the PM6:TZ2 device, longer than 55 μ s for the PM6:TZ1 device, implying PM6:TZ2 devices possess less carrier recombination [41]. All these results support the higher J_{sc} of PM6:TZ2 device (see Fig. 3).

2.5. Morphology analysis

The morphology of the blend films were charcterized by transmission electron microscopy (TEM) and atomic force microscopy (AFM). As shown in Fig. 5a and b, in comparison with PM6:TZ1 blend film, the PM6:TZ2 blend film shows more distinct fibrous network and forms bicontinuous-interpenetrating network of polymer donors and acceptors, which is beneficial for exciton dissociation, charge transportation, and reducing charge recombination [21,42,43]. Besides, compared with the PM6:TZ1 blend film with root-mean-square (RMS) roughness of 2.29 nm, the PM6:TZ2 blend film shows a rougher surface with larger RMS roughness of 3.70 nm, which might be caused by the stronger molecular aggregation behavior of TZ2. These results suggest that the introduction of F atoms into the backbone of nonlinear π -conjugated polymer acceptors enhance the aggregation ability and promote the phase separation between polymer donor and polymer acceptor.

3. Conclusions

In this work, we proposed a new strategy for the synthesis of nonlinear π -conjugated polymer acceptors (NLCPAs). By choosing different linkage units, two novel nonlinear π -conjugated polymer materials (namely TZ1 and TZ2) with various properties were successfully obtained. TZ1 and TZ2 exhibit wide and efficient absorption and suitable energy levels as the electron acceptors. In comparison with the nonfluorinated polymer acceptor TZ1, the fluorinated polymer acceptor TZ2 presents lower energy level, strong molecular aggregation and thus higher carrier mobilities. After blending with PM6, both polymer acceptors-based devices offered V_{oc} over 0.92 V. However, compared



Fig. 4. (a) J_{sc} vs. light intensity of PM6:TZ1 and PM6:TZ2; (b) V_{oc} vs. light intensity of PM6:TZ1 and PM6:TZ2; (c) TPC and (d) TPV measurements of PM6:TZ1 and PM6:TZ2.



Fig. 5. (a) TEM image of PM6:TZ1; (b) TEM image of PM6:TZ2; (c) AFM height images of PM6:TZ1; (d) AFM height images of PM6:TZ2.

with TZ1-based device, the TZ2-based device achieved a better PCE of 7.41%, which can be attributed to its obviously higher J_{sc} of 14.94 mA cm⁻². Our work points to the importance of fluorination for NLCPAs and provides guidelines for the design of efficient NLCPAs. Considering the diverse of linkage units and the central cores, the emergence of nonlinear π -conjugated polymer acceptors with better performance is anticipating.

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.

Acknowledgment

The authors gratefully acknowledge the financial support from NSFC (21935007, 52025033, 51873089, 52073056) and MoST (2019YFA0705900) of China, Tianjin city (20JCZDJC00740), 111 Project (B12015), the 100 Young Academic Leaders Program of Nankai University (023-ZB22000105).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.orgel.2022.106735.

References

- S. Ma, H. Zhang, K. Feng, X. Guo, Polymer acceptors for high-performance allpolymer solar cells, Chem. Eur J. 28 (2022), e202200222.
- [2] H. Yin, C. Yan, H. Hu, J.K.W. Ho, X. Zhan, G. Li, S.K. So, Recent progress of allpolymer solar cells-From chemical structure and device physics to photovoltaic performance, Mater. Sci. Eng. R. 140 (2020), 100542.
- [3] K. Zhou, K. Xian, L. Ye, Morphology control in high-efficiency all-polymer solar cells, Info 4 (2022) e1227.
- [4] G. Wang, F.S. Melkonyan, A. Facchetti, T.J. Marks, All-polymer solar cells: recent progress, challenges, and prospects, Angew. Chem., Int. Ed. 58 (2019) 4129–4142.
- [5] H. Yao, J. Hou, Recent advances in single-junction organic solar cells, Angew. Chem., Int. Ed. (2022), e202209021.
- [6] J. Wang, Y. Cui, Y. Xu, K. Xian, P. Bi, Z. Chen, K. Zhou, L. Ma, T. Zhang, Y. Yang, Y. Zu, H. Yao, X. Hao, L. Ye, J. Hou, A new polymer donor enables binary allpolymer organic photovoltaic cells with 18% efficiency and excellent mechanical robustness, Adv. Mater. (2022), e2205009.
- [7] Y. Cui, Y. Xu, H. Yao, P. Bi, L. Hong, J. Zhang, Y. Zu, T. Zhang, J. Qin, J. Ren, Z. Chen, C. He, X. Hao, Z. Wei, J. Hou, Single-Junction organic photovoltaic cell with 19% efficiency, Adv. Mater. 33 (2021), e2102420.
- [8] Q. Yang, W. Yu, J. Lv, P. Huang, G. He, Z. Xiao, Z. Kan, S. Lu, Effects of fluorination position on all-polymer organic solar cells, Dyes Pigments 200 (2022), 110180.
- [9] R. Sun, W. Wang, H. Yu, Z. Chen, X. Xia, H. Shen, J. Guo, M. Shi, Y. Zheng, Y. Wu, W. Yang, T. Wang, Q. Wu, Y. Yang, X. Lu, J. Xia, C.J. Brabec, H. Yan, Y. Li, J. Min, Achieving over 17% efficiency of ternary all-polymer solar cells with two wellcompatible polymer acceptors, Joule 5 (2021) 1548–1565.
- [10] Y. Li, J. Song, Y. Dong, H. Jin, J. Xin, S. Wang, Y. Cai, L. Jiang, W. Ma, Z. Tang, Y. Sun, Polymerized small molecular acceptor with branched side chains for all polymer solar cells with efficiency over 16.7%, Adv. Mater. 34 (2022), e2110155.
- [11] H. Yu, Y. Wang, H.K. Kim, X. Wu, Y. Li, Z. Yao, M. Pan, X. Zou, J. Zhang, S. Chen, D. Zhao, F. Huang, X. Lu, Z. Zhu, H. Yan, A vinylene-linker-based polymer acceptor featuring a coplanar and rigid molecular conformation enables high-performance all-polymer solar cells with over 17% efficiency, Adv. Mater. 34 (2022), e2200361.
- [12] H. Yang, H. Fan, Z. Wang, H. Yan, Y. Dong, C. Cui, H. Ade, Y. Li, Impact of isomer design on physicochemical properties and performance in high-efficiency allpolymer solar cells, Macromolecules 53 (2020) 9026–9033.
- [13] H. Yang, S. Bao, H. Fan, C. Fan, X. Zhu, C. Cui, Y. Li, Molecular Optimization on Polymer Acceptor Enables Efficient All-Polymer Solar Cell with High Open-Circuit Voltage of 1.10 V, Macromol Rapid Commun, 2022, e2100925.
- [14] X. Zhan, Z.a. Tan, B. Domercq, Z. An, X. Zhang, S. Barlow, Y. Li, D. Zhu, B. Kippelen, S.R. Marder, A high-mobility electron-transport polymer with broad absorption and its use in field-effect transistors and all-polymer solar cells, J. Am. Chem. Soc. 129 (2007) 7246–7247.
- [15] H. Yan, Z. Chen, Y. Zheng, C. Newman, J.R. Quinn, F. Dotz, M. Kastler, A. Facchetti, A high-mobility electron-transporting polymer for printed transistors, Nature 457 (2009) 679–686.
- [16] M.F. Falzon, A.P. Zoombelt, M.M. Wienk, R.A. Janssen, Diketopyrrolopyrrolebased acceptor polymers for photovoltaic application, Phys. Chem. Chem. Phys. 13 (2011) 8931–8939.
- [17] R. Stalder, J. Mei, J. Subbiah, C. Grand, L.A. Estrada, F. So, J.R. Reynolds, n-Type conjugated polyisoindigos, Macromolecules 44 (2011) 6303–6310.
- [18] X. Long, Z. Ding, C. Dou, J. Zhang, J. Liu, L. Wang, Polymer acceptor based on double B←N bridged bipyridine (BNBP) unit for high-efficiency all-polymer solar cells, Adv. Mater. 28 (2016) 6504–6508.
- [19] Z.G. Zhang, Y. Li, Polymerized small-molecule acceptors for high-performance allpolymer solar cells, Angew. Chem., Int. Ed. 60 (2021) 4422–4433.
- [20] Z.G. Zhang, Y. Yang, J. Yao, L. Xue, S. Chen, X. Li, W. Morrison, C. Yang, Y. Li, Constructing a strongly absorbing low-bandgap polymer acceptor for high-

performance all-polymer solar cells, Angew. Chem., Int. Ed. 56 (2017) 13503–13507.

- [21] J. Du, K. Hu, J. Zhang, L. Meng, J. Yue, I. Angunawela, H. Yan, S. Qin, X. Kong, Z. Zhang, B. Guan, H. Ade, Y. Li, Polymerized small molecular acceptor based allpolymer solar cells with an efficiency of 16.16% via tuning polymer blend morphology by molecular design, Nat. Commun. 12 (2021) 5264.
- [22] D. Zhou, C. Liao, S. Peng, X. Xu, Y. Guo, J. Xia, H. Meng, L. Yu, R. Li, Q. Peng, Binary blend all-polymer solar cells with a record efficiency of 17.41% enabled by programmed fluorination both on donor and acceptor blocks, Adv. Sci. 9 (2022), e2202022.
- [23] T. Jarosz, M. Lapkowski, P. Ledwon, Advances in star-shaped pi-conjugated systems: properties and applications, Macromol, Rapid Commun 35 (2014) 1006–1032.
- [24] J. Ji, L. Zhu, X. Xiong, F. Liu, Z. Liang, Developing Y-branched polymer acceptor with 3D architecture to reconcile between crystallinity and miscibility yielding >15% efficient all-polymer solar cells, Adv. Sci. 9 (2022), e2200864.
- [25] F. Liu, J.Q. Liu, R.R. Liu, X.Y. Hou, L.H. Xie, H.B. Wu, C. Tang, W. Wei, Y. Cao, W. Huang, Hyperbranched framework of interrupted π-conjugated polymers endcapped with high carrier-mobility moieties for stable light-emitting materials with low driving voltage, J. Polym. Sci., Part A: Polym. Chem. 47 (2009) 6451–6462.
- [26] W. Jiang, Y. Zhou, D. Yan, Hyperbranched polymer vesicles: from self-assembly, characterization, mechanisms, and properties to applications, Chem. Soc. Rev. 44 (2015) 3874–3889.
- [27] J. Li, Z. Bo, "AB2 + AB" approach to hyperbranched polymers used as polymer blue light emitting materials, Macromolecules 37 (2004) 2013–2015.
- [28] X. Li, H. Zhao, L. Gao, X. Xie, W. Zhang, M. Wang, Y. Wu, Y. Miao, H. Wang, B. Xu, Synthesis and properties of hyperbranched polymers for white polymer lightemitting diodes, RSC Adv. 9 (2019) 36058–36065.
- [29] H. Chen, H. Liang, Z. Guo, Y. Zhu, Z. Zhang, Z. Li, X. Cao, H. Wang, W. Feng, Y. Zou, L. Meng, X. Xu, B. Kan, C. Li, Z. Yao, X. Wan, Z. Ma, Y. Chen, Central unit fluorination of non-fullerene acceptors enables highly efficient organic solar cells with over 18 % efficiency, Angew. Chem., Int. Ed. 61 (2022), e202209580.
- [30] H. Yu, M. Pan, R. Sun, I. Agunawela, J. Zhang, Y. Li, Z. Qi, H. Han, X. Zou, W. Zhou, S. Chen, J. Y.L. Lai, S. Luo, Z. Luo, D. Zhao, X. Lu, H. Ade, F. Huang, J. Min, H. Yan, Regio-regular polymer acceptors enabled by determined fluorination on end groups for all-polymer solar cells with 15.2 % efficiency, Angew. Chem., Int. Ed. 60 (2021) 10137–10146.
- [31] H. Chen, Y. Zou, H. Liang, T. He, X. Xu, Y. Zhang, Z. Ma, J. Wang, M. Zhang, Q. Li, C. Li, G. Long, X. Wan, Z. Yao, Y. Chen, Lowing the energy loss of organic solar cells by molecular packing engineering via multiple molecular conjugation extension, Sci. China Chem. 65 (2022) 1362–1373.
- [32] Y. Zou, H. Chen, X. Bi, X. Xu, H. Wang, M. Lin, Z. Ma, M. Zhang, C. Li, X. Wan, G. Long, Y. Zhaoyang, Y. Chen, Peripheral halogenation engineering controls molecular stacking to enable highly efficient organic solar cells, Energy Environ. Sci. 15 (2022) 3519–3533.
- [33] R. Steyrleuthner, M. Schubert, I. Howard, B. Klaumunzer, K. Schilling, Z. Chen, P. Saalfrank, F. Laquai, A. Facchetti, D. Neher, Aggregation in a high-mobility ntype low-bandgap copolymer with implications on semicrystalline morphology, J. Am. Chem. Soc. 134 (2012) 18303–18317.
- [34] H. Yamagata, F.C. Spano, Interplay between intrachain and interchain interactions in semiconducting polymer assemblies: the HJ-aggregate model, Appl. Phys. Lett. 136 (2012), 184901.
- [35] F. Panzer, H. Bassler, A. Kohler, Temperature induced order-disorder transition in solutions of conjugated polymers probed by optical spectroscopy, J. Phys. Chem. Lett. 8 (2017) 114–125.
- [36] X. Wan, C. Li, M. Zhang, Y. Chen, Acceptor-donor-acceptor type molecules for high performance organic photovoltaics - chemistry and mechanism, Chem. Soc. Rev. 49 (2020) 2828–2842.
- [37] G. Han, Y. Yi, Molecular insight into efficient charge generation in low-drivingforce nonfullerene organic solar cells, Acc. Chem. Res. 55 (2022) 869–877.
- [38] C.M. Proctor, J.A. Love, T.Q. Nguyen, Mobility guidelines for high fill factor solution-processed small molecule solar cells, Adv. Mater. 26 (2014) 5957–5961.
- [39] S.R. Cowan, A. Roy, A.J. Heeger, Recombination in polymer-fullerene bulk heterojunction solar cells, Phys. Rev. B 82 (2010), 245207.
- [40] L.J.A. Koster, V.D. Mihailetchi, R. Ramaker, P.W.M. Blom, Light intensity dependence of open-circuit voltage of polymer:fullerene solar cells, Appl. Phys. Lett. 86 (2005).
- [41] M. Babics, R.-Z. Liang, K. Wang, F. Cruciani, Z. Kan, M. Wohlfahrt, M.-C. Tang, F. Laquai, P.M. Beaujuge, Solvent vapor annealing-mediated crystallization directs charge generation, recombination and extraction in BHJ solar cells, Chem. Mater. 30 (2018) 789–798.
- [42] L. Zhu, M. Zhang, J. Xu, C. Li, J. Yan, G. Zhou, W. Zhong, T. Hao, J. Song, X. Xue, Z. Zhou, R. Zeng, H. Zhu, C.C. Chen, R.C.I. MacKenzie, Y. Zou, J. Nelson, Y. Zhang, Y. Sun, F. Liu, Single-junction organic solar cells with over 19% efficiency enabled by a refined double-fibril network morphology, Nat. Mater. 21 (2022) 656–663.
- [43] Z. Wang, K. Gao, Y. Kan, M. Zhang, C. Qiu, L. Zhu, Z. Zhao, X. Peng, W. Feng, Z. Qian, X. Gu, A.K. Jen, B.Z. Tang, Y. Cao, Y. Zhang, F. Liu, The coupling and competition of crystallization and phase separation, correlating thermodynamics and kinetics in OPV morphology and performances, Nat. Commun. 12 (2021) 332.