Rational Design of Conjugated Polymers for \(d\)-Limonene Processed All-polymer Solar Cells with Small Energy Loss

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Electronic Supplementary Information

**Abstract** In this work, we designed and synthesized a novel naphthalenediimide-based n-type conjugated polymer PNDICl, which bears asymmetric backbone containing a 3-chlorothiophene unit. The asymmetric structure associated with steric effects of the chlorine atom imparts remarkable solubility to PNDICl in various organic solvents, enabling the fabrication of all-polymer solar cells (all-PSCs) by using an environmentally friendly solvent of \(d\)-limonene. Combined with a novel pyrrolo[3,4-f]benzotriazole-5,7(6H)-dione based p-type conjugated polymer P2F-Si with deep highest occupied molecular orbital energy level, the resulting \(d\)-limonene-processed all-PSCs presents an impressively high open-circuit voltage of approaching 1.0 V, corresponding to a very small energy loss of 0.49 eV. Through further morphology optimization by using \(y\)-valerolactone, we demonstrated an impressive device efficiency of 4.2%, which is among the best photovoltaic performance of devices processed using \(d\)-limonene and comparable to that processed by conventional solvent, suggesting the great promise of using greener solvent for fabricating high-performance all-PSCs.

**Keywords** All-polymer solar cells; Chlorination; Environmentally friendly solvent; High open-circuit voltage; Small energy loss

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**INTRODUCTION**

Polymer solar cells (PSCs) have attracted tremendous attention owning to their unique merits of low-cost, solution-production, and mechanical flexibility.\(^1\)–\(^9\) The state-of-the-art PSCs have realized impressive power conversion efficiencies (PCEs) of over 16%,\(^10\)–\(^14\) mitigating the gap regarding to other emerging photovoltaic techniques. In addition to developing PSCs toward large-scale roll-to-roll production,\(^15,16\) numerous efforts have been devoted to all-polymer solar cells (all-PSCs),\(^17\)–\(^23\) which include both p-type and n-type polymers in the light-harvesting layer.\(^24\)–\(^32\) While most all-PSCs are processed using toxic halogenated solvents, much interest has been devoted to seeking non-toxic, environmentally benign processing solvents toward large-scale clean production. In this regard, a variety of non-halogenated solvents, such as toluene, 1,2,4-trimethylbenzene, tetrahydrofuran, methoxymethylene, 2-methylytetrafluoruran (MeTHF), and cyclopentyl methyl ether (CPME) were thus employed.\(^33\)–\(^39\)

Among the reported non-aromatic solvents, the ether solvents such as MeTHF or CPME are much appreciated, since they can enable pre-aggregation of polymer chains in solution due to its moderate solubility, and thus lead to highly-aligned polymer films that are favorable for inter-molecular charge transport.\(^40\)–\(^41\) In comparison to those aforementioned non-halogenated and non-aromatic solvents, \(d\)-limonene (LM, Fig. 1a) is much more environmentally friendly, since it is originated from the peel of citrus fruits and can be used as a flavoring agent in food.\(^42\) However, the application of LM for processing conjugated polymers is limited, because most conjugated polymers with rigid backbone can be barely dissolved in LM (Fig. S1 and Table S1, in the electronic supplementary information, ESI).

To fabricate all-PSCs using LM, we herein developed a novel n-type polymer, poly[(\(N,N\)-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl)-alt-5,5'-(3\(′\)-chloro-2,2'‑bithiophen)] (PNDICl, Fig. 1a), which has an asymmetric structure containing a chlorinated thiophene on the main chain. Considering that the chlorine substitution generally leads to down-shifted lowest-unoccupied molecular orbital (LUMO) energy level of the resulting polymers, the resulting devices may attain reduced open-circuit voltage (\(V_{oc}\)).\(^43\) To address this issue, we correspondingly developed a novel p-type polymer, namely P2F-Si (Fig. 1a), which con-
tains a pyrrolo[3,4-f]benzotriazole-5,7(6H)-dione (TzBI) skeleton with a siloxane-ended alkyl-side chain. The electron-deficient TzBI unit presented similarly moderate electron-withdrawing capability regarding to the difluorinated benzotriazole unit, yet the imide-group allowed for the incorporation of an additional solubilizing group that can impart excellent solubility of the resulting group.

Moreover, the siloxane moiety was incorporated as the end-group of the side chain because it can further enhance the solubility without disturbing the intermolecular stacking regarding to the branched alkyl-side chains.

It is also worth noting that the electron-withdrawing difluorophenyl substituents of benzo[1,2-b:4,5-b']dithiophene can result in decreased highest occupied molecular orbital (HOMO) energy level, which can potentially compensate for the possibly decreased $V_{OC}$ derived from the slightly down-shifted LUMO energy level of PNDICI.

Of particular importance is that both P2F-Si and PNDICI can be easily dissolved in LM (b.p. ~177 °C, Table S2 in ESI). The resulting all-PSCs presented an impressively high $V_{OC}$ of approaching 1.0 V, associating with a relatively small energy loss of 0.49 eV. Through a morphology optimization strategy by using a non-halogenated solvent additive of $\gamma$-valerolactone (VA, Fig. 1a), a decent efficiency of 4.18% is achieved, suggesting the great promise of using greener solvent for fabricating high-performance all-PSCs.

**RESULTS AND DISCUSSION**

**Synthesis and Characterization of Materials**

The synthetic routes of the polymers are summarized in Scheme 3.
S1 (in ESI) with relevant structures confirmed by proton nuclear magnetic resonance (Figs. S2–S4 in ESI). Density functional theory simulation (B3LYP/6-31G (d, p)) indicated that the chloride on thiophene leads to enlarged dihedral angle to 57.29° (Fig. S5 in ESI), presenting more pronounced twisted skeleton than that of counterpart copolymer N2200. The asymmetric structure of PNDICI enabled remarkable solubility in green solvent LM (Fig. S1 and Table S1 in ESI). The number-average molecular weight of P2F-Si and PNDICI was estimated to be 17.9 and 31.7 kDa, respectively. Differential scanning calorimetry demonstrated that PNDICI exhibited a sharp crystallization transition at 295 °C (Fig. S6b in ESI), while P2F-Si did not present discernible thermal transition up to 300 °C (Fig. S6a in ESI).

**Photoelectrical Properties**

The HOMO/LUMO energy levels of PNDICI and P2F-Si were estimated to be −5.98/−3.89 eV and −5.51/−3.13 eV, respectively, by cyclic voltammetry measurement (Fig. S7a in ESI). The HOMO of P2F-Si was slightly deeper than that of PNDICI. While the LUMO energy level of PNDICI was estimated to be −17.9 and 31.7 kDa, respectively, by cyclic voltammetry measurement (Fig. S7a in ESI). The combination of these variations would lead to enhanced $V_{OC}$ of P2F-Si:PNDICI than that of PTzBi-Si:N2200. The UV-Vis absorption spectra for PTzBi-Si, P2F-Si, and PNDICI neat films processed by different solvents are illustrated in Fig. 1(c) and Fig. S8 (in ESI). For all three polymers, LM-cast films show enhanced shoulder peaks regarding to those casted from MeTHF- and CPME-solution (Fig. S8 in ESI), which should be attributable to the polymer pre-aggregation in LM. The optical bandgap ($E_{gopt}$) of these LM-processed polymers was estimated by Tauc plots (Fig. S7b, in ESI), where we note that PNDICI exhibits a slightly larger $E_{gopt}$ (1.48 eV) than N2200 ($E_{gopt} = 1.46$ eV), which can be ascribed to the decreased intra-molecular charge transfer induced by chloride substitution.

**Photovoltaic Performance**

To investigate the impact of processing solvent on photovoltaic performance, we fabricated all-PSCs with structure of ITO/PEDOT:PSS/photoactive layer/PFNDI-Br/Ag, where PFNDI-Br (~5 nm) was employed to facilitate the electron extraction (Fig. 1a). Since we focused on the processing solvent, the weight ratio of the photoactive layer consisting of donor:acceptor was settled as 2:1 with a fixed thickness of ~100 nm. We also simplified the post-treatments by only thermal annealing at 100 °C for 10 min. The J-V characteristics for all-PSC devices processed by different solvents are depicted in Fig. 2(a), with the corresponding photovoltaic parameters summarized in Table 1.

The control device based on PTzBi-Si:PNDICI processed by CPME presents a $V_{OC}$ of 0.81 V, a short-circuit current ($J_{SC}$) of 10.6 mA·cm$^{-2}$, and a fill factor (FF) of 63.5%, corresponding to a PCE of 5.4%. In contrast, the LM-processed device exhibits a much higher FF of 72.7% while exhibits an obviously de-

![Fig. 2](https://doi.org/10.1007/s10118-020-2429-3)
creased $J_{SC}$ of 5.1 mA·cm$^{-2}$, giving a moderate efficiency of 3.0%. This observation is different for the P2F-Si:PNDCI system, where CPME- and LM-processed devices present similar photovoltaic performance. By exploiting a low-toxic additive of γ-valerolactone (Table S2 in ESI), the LM-processed device presents an optimal power conversion efficiency of 4.2% ($V_{OC} = 0.99$ V, $J_{SC} = 6.6$ mA·cm$^{-2}$, FF = 64.0%, Table S4 and Fig. S9 in ESI). Note that an impressive $V_{SC}$ approaching 1 V was achieved in this system, demonstrating the validity of decreasing the HOMO energy level of donor toward high $V_{OC}$. The energy loss ($E_{loss}$) was calculated according to the formula of $E_{loss} = E_g - E_{min}$, where $E_{min}$ is the minimal $E_g$ between donor and acceptor (Table S3 in ESI). As listed in Table 1, the LM-processed P2F-Si:PNDCI device has a fairly small $E_{loss}$ of 0.49 eV, much lower than that for PTzBI-Si-based device ($E_{loss} = 0.68$ eV). Importantly, compared with the devices processed with CPME, devices processed by LM show an obviously increased FF and slightly decreased $J_{SC}$ in both P2F-Si:PNDCI and PTzBI-Si:PNDCI systems. The external quantum efficiency (EQE, Fig. 2b) and the integrated current density (Table 1) confirm the reliability of $J_{SC}$ obtained from the J-V measurement system.

To correlate the $J_{SC}$ and FF difference in these devices, we measured the absorption of blend films processed with different solvents. As shown in Fig. S10 (in ESI), one noted an enhanced shoulder peak at 620 and 605 nm attributed to PTzBI-Si and P2F-Si, respectively, for LM-processed blends relative to the MeTHF- and CPME-cases, implying that the polymer pre-aggregation also existed in blend solution. This may contribute to the formation of highly-aligned blend-films and thus account for the much higher FF of LM-processed all-PSCs. However, no obvious difference was discerned in the near-infrared (NIR) region (> 700 nm) that exclusively correlated to the absorption of PNDCI, which can be attributed to the under-estimation of NIR absorption of PNDCI by transmission method. Considering the reflection ($R$), we depicted the device absorption ($1 - R$) in Fig. 2(c), where we note a significantly enhanced absorption in the range of 670−750 nm for P2F-Si:PNDCI-based device, while the PTzBI-Si:PNDCI device maintains a relatively low NIR-absorption ($1 - R$) that accounts for its poor $J_{SC}$.

Photoluminescence spectroscopy (PL) was also used to shed light on the difference of current densities, with the thickness of all films fixed as 95 ± 5 nm. As shown in Fig. 2(d), LM-cast neat-film of PTzBI-Si and P2F-Si exhibits a peak at 713 and 690 nm (excited at 580 nm), respectively. Note that the PL intensity of P2F-Si is much higher than that of PTzBI-Si under the same test condition (slit width = 5 nm). After blended with PNDCI, the PL peak of P2F-Si is effectively quenched. In contrast, the quench of PTzBI-Si emission is much less pronounced for the films processed with both CPME- and LM-solution. These observations demonstrate the weak charge transfer in PTzBI-Si:PNDCI-system, especially for the LM-processed films. Additionally, for both systems, the LM-films show less-efficient PL-quenching than the CPME-counterparts, indicating quite different phase-separated morphology for these blend films (Table 1). The emission quenching of acceptor was investigated with all films excited at 710 nm. As shown in Fig. S11 (in ESI), the quenching behavior is very similar to that observed for donors.

**Morphology Analysis**

Atom force microscopy (AFM) was used to reveal the surface morphology of blend films. For P2F-Si:PNDCI, CPME-processed film exhibits a smooth surface with a low root-mean-square (RMS) roughness value of 1.5 nm (Fig. S12a in ESI), whereas LM-processing gives large aggregates and much higher RMS roughness of 5.4 nm (Fig. S12b in ESI). Interestingly, the incorporation of 0.5% volume ratio of γ-valerolactone into LM significantly reduces the aggregates and decreases the roughness to 2.5 nm (Fig. S12c in ESI), leading to the improved $J_{SC}$. Note that PTzBI-Si:PNDCI-films show very thick fibers on the surface, especially in the LM-processed case (Figs. S12d and S12e in ESI). The well-organized morphology might contribute to the measured high FF of the resulting devices.

We further conducted the two-dimensional (2D) grazing incidence X-ray diffraction (GIXD) to understand the role of processing solvent in crystalline structures. From the GIXD patterns of neat films processed by LM, we note an evident $n-n$ stacking (010) signal in the out-of-plane (OOP) direction, together with a corresponding in-plane (IP) lamellar stacking (100) peak for both P2F-Si and PNDCI. As shown in Fig. S3 in ESI, PTzBI-Si:PNDCI films show slightly thicker fibers with the (010) peak shifted to a higher position at $q = 1.71$ Å$^{-1}$ and a crystal coherent length (CCL) of 17.1 Å (Fig. 3a and Fig. 3b in ESI). The GIXD processing gives slightly different scattering textures with the (010) peak shifted towards a higher $q$ position at 1.73 Å$^{-1}$ and the CCL increased to 21.0 Å (Table S5 in ESI), indicating a more compact $n-n$ co-facial packing and an increased crystal grain size. However, the (010) reflection arc also extends from OOP direction towards the in-plane (IP) direction (Fig. S13 in ESI), suggesting that a certain amount of $n-n$ stacking was switched from face-on to random arrangement during the LM processing. The incorporation of γ-valerolactone as the solvent additive did not significantly alter the (010) peak, while the (100), (200), and (300) lamellar stacking peaks were mainly centered to OOP direction, implying the ordered side-chain stacking. The improved crystallites embedded in bulk heterojunction (BHJ) framework can facilitate the charge movement and ultimately enhance the fill factor.}

### Table 1: Photovoltaic parameters for all-PSCs processed with different solvents.

| Blend          | Solvent  | $V_{OC}$ (V) | $J_{SC}$ (mA·cm$^{-2}$) | $J_{SC,EQE}$ (mA·cm$^{-2}$) | FF (%) | PL quenching (%) | PCE (%) |
|---------------|----------|--------------|------------------------|-----------------------------|--------|------------------|--------|
| PTzBI-Si:PNDCI| CPME     | 0.81         | 10.6 (9.8 ± 0.5)       | 9.7                         | 63.5   | (65.2 ± 1.2)    | 85.9   |
|               | LM       | 0.80         | 5.1 (4.9 ± 0.1)        | 4.8                         | 72.7   | (71.6 ± 1.1)    | 43.6   |
| P2F-Si:PNDCI  | CPME     | 0.97         | 8.0 (7.8 ± 0.2)        | 7.7                         | 58.5   | (57.7 ± 0.9)    | 97.3   |
|               | LM       | 0.99         | 6.6 (6.6 ± 0.2)        | 6.2                         | 64.0   | (63.9 ± 0.4)    | 83.4   |

* Incorporating 0.5 vol% γ-valerolactone (VA) as the solvent additive. Data in the parentheses are the statistical values obtained from 12 devices.
Resonant soft x-ray scattering (RSoXS) was also utilized to correlate the phase separation structure with the solar cell efficiency. The RSoXS circularly integrated profiles at beam energy of 285.2 eV are collected in Fig. 3(b). The CPME-processed blend film shows poor compositional contrast with a hump at \( q \approx 0.0044 \text{ Å}^{-1} \), corresponding to a statistic inter-domain size of 142 nm. When using LM as the processing solvent, the hump is broadened and shifts to 0.0068 Å\(^{-1}\) (domain size \( \sim 93 \text{ nm} \)) with the scattering intensity significantly increasing over the \( q \) vector, while additional 0.5% \( \gamma \)-valerolactone leads to a slightly higher domain size of 110 nm (\( q = 0.0057 \text{ Å}^{-1} \)). These results demonstrate that using LM for film deposition can decrease the phase separation and meantime lead to higher relative phase purity. The lower disperse of the polymers induced by the increased crystallinity is detrimental to the exciton splitting,\(^{[46]}\) thus decreasing the PL quenching efficiency (Fig. 2d and Table 1), which agrees well with the slightly decreased \( J_{SC} \) of LM-devices.

CONCLUSIONS

In summary, we designed and synthesized a novel naphtha-lenediimide based polymeric acceptor (PNDICl) containing a chlorinated thiophene in the backbone, and a novel pyrrolo[3,4-\( \beta \)]benzotriazole-5,7(6H)-dione based polymeric donor (P2F-Si) containing a benzo[1,2-b:4,5-b']dithiophene derivative in the backbone. The resulting polymer can be readily dissolved in \( d \)-limonene, enabling the fabrication of all-PSCs by using a green solvent. Benefiting from the deep highest occupied molecular orbital energy level of P2F-Si, the all-PSC based on P2F-SI:PNDICl as the photoactive layer processed by \( d \)-limonene exhibits an impressively high open-circuit voltage of approaching 1.0 V, corresponding to a very small energy loss of 0.49 eV. Further morphology optimization by using a green solvent additive, \( \gamma \)-valerolactone, demonstrated a reasonable power conversion efficiency of 4.2%, which is comparable with that processed by conventional solvent of cyclopentyl methyl ether. These observations clearly suggested that green solvent of \( d \)-limonene has great promise for fabricating high-performance all-PSCs.

**Electronic Supplementary Information**

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-020-2429-3.

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**REFERENCES**

1. Lee, C.; Lee, S.; Kim, G. U.; Lee, W.; Kim, B. J. Recent advances, design guidelines, and prospects of all-polymer solar cells. **Chem. Rev.** 2019, 119, 8028–8086.
2. Yan, C.; Barlow, S.; Wang, Z.; Yan, H.; Jen, A. K. Y.; Marder, S. R.; Zhan, X. Non-fullerene acceptors for organic solar cells. **Nat. Rev. Mater.** 2018, 3, 18003.
3. Li, Z.; Zhong, W.; Ying, L.; Li, F.; Li, N.; Huang, F.; Cao, Y. Morphology optimization via molecular weight tuning of donor polymer enables all-polymer solar cells with simultaneously improved performance and stability. **Nano Energy** 2019, 64, 103931.
4. Li, Z.; Zhong, W.; Ying, L.; Li, N.; Liu, F.; Huang, F.; Cao, Y. Achieving efficient thick film all-polymer solar cells using a green solvent additive. **Chinese J. Polym. Sci.** 2020, 38, 323–331.
5. Zhao, R.; Dou, C.; Liu, J.; Wang, L. An alternating polymer of two building blocks based on 8–B–N unit: non-fullerene acceptor for organic photovoltaics. **Chinese J. Polym. Sci.** 2017, 35, 198–206.
6. Huo, Y.; Zhang, H. L.; Zhan, X. Nonfullerene all-small-molecule organic solar cells. **ACS Energy Lett.** 2019, 4, 1241–1250.
7. Huang, F.; Bo, Z.; Geng, Y.; Wang, X.; Wang, L.; Ma, Y.; Hou, J.; Hu, W.; Pei, J.; Dong, H.; Wang, S.; Li, Z.; Shuai, Z.; Li, Y.; Cao, Y. Study on optoelectronic polymers: an overview and outlook. **Acta Polymerica Sinica** (in Chinese) 2019, 50, 988–1046.
8. Zhong, W.; Xie, R.; Ying, L.; Huang, F.; Cao, Y. High performance polymer photodetectors enabled by a naphtho-[1,2-c:5,6-c']bis[1,2,5]thiadiazole based \( \pi \)-conjugated polymer. **Acta Polymerica Sinica** (in Chinese) 2018, 217–222.
9. Dang, D.; Chen, W.; Himmelberger, S.; Tao, Q.; Lundin, A.; Yang, R.; Zhu, W.; Salleo, A.; Müller, C.; Wang, E. Enhanced photovoltaic performance of indacenodithiophene-quinoxaline copolymers by side-chain modulation. **Adv. Energy Mater.** 2014, 4, 1400680.
10. Fan, B.; Zhang, D.; Li, M.; Zhong, W.; Zeng, Z.; Ying, L.; Huang, F.; Cao, Y. Achieving over 16% efficiency for single-junction organic solar cells. **Sci. China Chem.** 2019, 62, 746–752.
11. An, Q.; Ma, X.; Gao, J.; Zhang, F. Solvent additive-free ternary polymer solar cells with 16.27% efficiency. **Sci. Bull.** 2019, 64, 504.
12. Yan, T.; Song, W.; Huang, J.; Peng, R.; Huang, L.; Ge, Z. 16.67% rigid and 14.06% flexible organic solar cells enabled by ternary heterojunction strategy. **Adv. Mater.** 2019, 31, 1902210.
13. Li, K.; Wu, Y.; Tang, Y.; Pan, M. A.; Ma, W.; Fu, H.; Zhan, C.; Yao, J. Ternary blended fullerene-free polymer solar cells with 16.5% efficiency enabled with a higher-LUMO-level acceptor to improve film morphology. **Adv. Energy Mater.** 2019, 9, 1901728.

https://doi.org/10.1007/s10118-020-2429-3
Xu, B.; Zhang, S.; Peng, J.; Wei, Z.; Gao, F.; Hou, J. Over 16% efficiency non-fullerene organic photovoltaic cells enabled by a chlorinated acceptor with increased open-circuit voltages. *Nat. Commun.* 2019, 10, 2515.

Xue, R.; Zhang, J.; Li, Y.; Li, Y. Organic solar cells materials toward commercialization. *Small* 2018, 14, 1801793.

Zhang, K.; Gao, K.; Xia, R.; Wu, Z.; Sun, C.; Cao, J.; Qian, L.; Li, W.; Liu, S.; Huang, F.; Peng, X.; Ding, L.; Yip, H.; Li; Cao, Y. High-performance polymer tandem solar cells employing a new n-type conjugated polymer as an interconnecting layer. *Adv. Mater.* 2016, 28, 4817–4823.

Zhang, M.; Ming, R.; Gao, W.; An, Q.; Ma, X.; Hu, Z.; Yang, C.; Zhang, F. Ternary polymer solar cells with alloyed non-fullerene acceptor with increased open-circuit voltages. *Acta Polymerica Sinica* (in Chinese) 2019, 50, 873–889.

Yuan, J.; Qiu, L.; Zhang, Z. G.; Li, Y.; Chen, Y.; Zou, Y. Tetrafluoroquinoxaline based polymers for non-fullerene polymer solar cells with efficiency over 9%. *Nano Energy* 2016, 30, 312–320.

Meng, B.; Miao, J.; Liu, J.; Wang, L. A new polymer electron acceptor based on thiophene-5,5-dioxide unit for organic photovoltaics. *Macromol. Rapid Commun.* 2018, 39, 1700505.

Chen, D.; Yao, J.; Chen, L.; Yin, J.; Li, R.; Huang, B.; Liu, S.; Zhang, Z. S.; Yang, C.; Chen, Y.; Li, Y. Dye-incorporated polythiophene-derivative acceptor for additive-free high-performance all-polymer solar cells. *Adv. Energy Mater.* 2018, 8, 1129–1138.

Zhang, L.; Xu, H.; Ding, Z.; Hu, J.; Liu, J.; Liu, Y. Amino N-oxide functionalized graphene quantum dots as a cathode interlayer for inverted polymer solar cells. *J. Mater. Chem. C* 2018, 6, 5684–5689.

Liu, J.; Wang, L. Polymer electron acceptors containing boron-nitrogen coordination bond (B–N) for all-polymer solar cells. *Acta Polymerica Sinica* (in Chinese) 2017, 1856–1869.

Zhaor, R.; Dou, C.; Xie, Z.; Liu, J.; Wang, L. Polymer acceptor based on B–N units with enhanced electron mobility for efficient all-polymer solar cells. *Angew. Chem. Int. Ed.* 2016, 55, 5313–5317.

Fan, B.; Zhong, W.; Yang, L.; Zhang, D.; Li, M.; Lin, Y.; Xia, R.; Liu, F.; Yip, H.; Li, Ming; Ma, Y.; Brabec, C.; Huang, F.; Cao, Y. Surpassing the 10% efficiency milestone for 1-cm2 all-polymer solar cells. *Nat. Commun.* 2019, 10, 1.

Gao, L.; Zhang, Z. G.; Xue, L.; Min, J.; Zhang, J.; Wei, Z.; Li, Y. All-polymer solar cells based on absorption-complementary polymer donor and acceptor with high power conversion efficiency of 8.27%. *Adv. Mater.* 2016, 28, 1884–1890.

Kolhe, N. B.; Tran, D. K.; Lee, H.; Kuzuhara, D.; Yoshimoto, N.; Koganazawa, T.; Jenekhe, S. A. New random copolymer acceptors enable additive-free processing of 10.1% efficient all-polymer solar cells with near-unity internal quantum efficiency. *ACS Energy Lett.* 2019, 4, 1162–1170.

Sun, H.; Tang, Y.; Koh, C. W.; Ling, S.; Wang, R.; Yang, K.; Yu, J.; Shi, Y.; Wang, Y.; Woo, H. Y.; Guo, X. High-performance all-polymer solar cells enabled by an n-type polymer based on a fluorinated imide-functionalized arene. *Adv. Mater.* 2019, 31, 1807202.

Xu, L.; Li, Z.; Zhang, W.; Meng, X.; Zou, X.; Di Carlo Rasi, D.; Ma, W.; Yartsev, A.; Andersson, M. R.; Jansen, R. A. J.; Wang, E. 8.0% Efficient all-polymer solar cells with high photovoltaic of 1.1 V and internal quantum efficiency near unity. *Adv. Energy Mater.* 2018, 8, 1700908.

Zhang, M.; Miao, D.; Zou, X.; Lin, B.; Wan, X.; Ma, W.; Chen, Y.; Long, X.; Dou, C.; Zhang, J.; Liu, J.; Wang, L. Efficient and thermally stable organic solar cells based on small molecule donor and polymer acceptor. *Nat. Commun.* 2019, 10, 3271.

He, Y.; Heumüller, T.; Lai, W.; Feng, G.; Classen, A.; Du, X.; Liu, C.; Li, W.; Li, N.; Brabec, C. J. Evidencing excellent thermal- and photo-stability for single-component organic solar cells with inherently built-In microstructure. *Adv. Energy Mater.* 2019, 9, 1900409.

Shi, Y.; Wang, Y.; Guo, X. Recent progress of inside-functionalized n-type polymer semiconductors. *Acta Polymerica Sinica* (in Chinese) 2019, 50, 873–889.

Ji, Y.; Xiao, C.; Wang, Q.; Zhang, J.; Li, C.; Wu, Y.; Wei, Z.; Xian, Z.; Hu, W.; Wang, Z.; Jassen, R. A. J.; Li, W. Asymmetric diketopyrrolopyrrole conjugated polymers for field-effect transistors and polymer solar cells processed from a nonchlorinated solvent. *Adv. Mater.* 2016, 28, 943–950.

Fan, B.; Ying, L.; Wang, Z.; He, B.; Jiang, X. F.; Huang, F.; Cao, Y. Optimisation of processing solvent and molecular weight for the production of green-solvent-processed all-polymer solar cells with a power conversion efficiency over 9%. *Energy Environ. Sci.* 2017, 10, 1243–1251.

Li, Z.; Ying, L.; Zhu, P.; Zhong, W.; Li, N.; Liu, F.; Huang, F.; Cao, Y. A generic green solvent concept boosting the power conversion efficiency of all-polymer solar cells to 11%. *Energy Environ. Sci.* 2019, 12, 157–163.

Chen, X.; Liu, X.; Burgers, M. A.; Huang, Y.; Bazan, G. C. Green-solvent-processed molecular organic solar cells. *Angew. Chem. Int. Ed.* 2014, 53, 14378–14381.

Xie, C.; Heumüller, T.; Gruber, W.; Tang, X.; Classen, A.; Schuldes, I.; Bidwell, M.; Speth, A.; Fink, R. H.; Unruh, T.; McCulloch, I.; Li, N.; Brabec, C. J. Overcoming efficiency and stability limits in water-processing nanoparticulate organic photovoltaics by minimizing microstructure defects. *Nat. Commun.* 2018, 9, 5335.

Farahat, M. E.; Perumal, P.; Budiawan, W.; Chen, Y.; Lee, C. H.; Heumüller, T.; Langbehn, T.; Tour, J. M. Generic green solvent concept boosting the power conversion efficiency of all-polymer solar cells to 10%. *Adv. Mater.* 2017, 29, 1703906.

Kim, N. K.; Kang, S. Y.; Pace, G.; Caironi, M.; Park, W. T.; Kim, J.; Kim, D. Y.; Yoo, Y. High-performance organic field-effect transistors with directionally aligned conjugated polymer film deposited from pre-aggregated solution. *Chem. Mater.* 2015, 27, 8345–8353.

Chu, C. W. Efficient molecular solar cells processed from green solvent mixtures. *J. Mater. Chem. A* 2017, 5, 571.

Meng, B.; Song, H.; Chen, X.; Xie, Z.; Liu, J.; Wang, L. Replacing alkylo(oxy)ethylene glycols as side chains of conjugated polymers for close n-n stacking. *Macromolecules* 2015, 48, 4357.

Fan, B.; Ying, L.; Zhu, P.; Pan, F.; Liu, J.; Chen, J.; Huang, F.; Cao, Y. All-polymer solar cells based on a conjugated polymer containing -o-thio-substitution. *Adv. Energy Mater.* 2018, 8, 1600960.

Fan, B.; Zhao, R.; Zhu, P.; Pan, F.; Liu, J.; Cao, Y.; Huang, F.; Cao, Y. High-performance all-polymer solar cells enabled by an n-type polymer donor for efficient organic solar cells. *Joule* 2018, 2, 1633–1634.

Fan, B.; Zhi, P.; Xin, J.; Li, N.; Ying, L.; Zhong, W.; Li, Z.; Ma, W.; Huang, F.; Cao, Y. High-performance thick-film all-polymer solar cells created via ternary blending of a novel wide-bandgap electron-donating copolymer. *Adv. Energy Mater.* 2018, 8, 1703085.

Zhong, W.; Hu, Q.; Jiang, Y.; Li, Y.; Chen, T. L.; Ying, L.; Liu, F.; Wang, C.; Liu, Y.; Huang, F.; Cao, Y.; Russell, T. P. In situ structure characterization in slot-die-printed all-polymer solar cells with efficiency over 6%. *Solar RRL* 2019, 3, 1900032.

Gao, K.; Peng, W.; Xiao, L.; Hu, Q.; Yan, Y.; Chen, X.; Wang, C.; Huang, F.; Peng, J.; Wu, H.; Peng, X.; Cao, Y.; Russell, T. P.; Liu, F. New insight of molecular interaction, crystallization and phase separation in higher performance small molecular solar cells via solvent vapor annealing. *Nano Energy* 2016, 30, 639–648.