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A Non-Conjugated Polymer Acceptor for Efficient and Thermally Stable All-Polymer Solar Cells

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Abstract: A non-conjugated polymer acceptor PF1-TS4 was firstly synthesized by embedding a thioalkyl segment in the mainchain, which shows excellent photophysical properties on par with a fully conjugated polymer, with a low optical band gap of 1.58 eV and a high absorption coefficient >10^6 cm⁻¹, a high LUMO level of ~3.89 eV, and suitable crystallinity. Matched with the polymer donor PM6, the PF1-TS4-based all-PSC achieved a power conversion efficiency (PCE) of 8.63%, which is ~45% higher than that of a device based on the small molecule acceptor counterpart IDIC16. Moreover, the PF1-TS4-based all-PSC has good thermal stability with ~70% of its initial PCE retained after being stored at 85°C for 180 h, while the IDIC16-based device only retained ~50% of its initial PCE when stored at 85°C for only 18 h. Our work provides a new strategy to develop efficient polymer acceptor materials by linkage of conjugated units with non-conjugated thioalkyl segments.

With the rapid development of high-performance non-fullerene small molecule (SM)-acceptors in the last five years,[1–2] the power conversion efficiencies (PCEs) of the state-of-the-art polymer solar cells (PSCs) have exceeded 7%,[3–5] mainly owing to their advantages of high absorption coefficients and good miscibility with polymer donors. However, the commercial application of PSCs is limited as their relatively low stability in many environmental issues, such as heat, oxygen, light, and humidity in outdoor can lead to device degradation.[7] Especially, the SM-acceptors tend to self-aggregate strongly, leading to poor morphological stability under heat from long-term solar irradiations, thus the related PSCs usually show poor thermal stability in device performance.[8] To address the thermal-instability of SM-acceptor-based active layers, some strategies, such as introducing volatile solid additives,[9] incorporating intermolecular...
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obtained a higher PCE of 8.63% with an almost unchanged and Table 1, respectively. The PF1-TS4-based all-PSCs based as-cast PSCs as a comparison are shown in Figure 1d and prevent chain alignment at a broad temperature range of C. Therefore, good thermal stability can be expected from such polymer-polymer blends.

To probe the photovoltaic performance of PF1-TS4, all-PSCs with a device structure of ITO/ZnO/PFN-Br/PM6:PF1-TS4/MoO3/Al were fabricated. Detailed optimization processes of the active layers are recorded in Figures S7–9 and Tables S1–3 (Supporting Information). The current density-voltage (J–V) plots and related photovoltaic parameters of the PF1-TS4-based optimized all-PSCs, as well as the IDIC16-based as-cast PSCs as a comparison are shown in Figure 1 d and Table 1, respectively. The PF1-TS4-based all-PSCs obtained a higher PCE of 8.63 % with an almost unchanged Voc of 0.98 V, a significantly increased Jsc of 15.04 mA cm⁻² and fill factor (FF) of 58.5 % compared to the IDIC16-based PSCs (PCE = 5.96 %, Voc = 0.99 V, Jsc = 11.80 mA cm⁻², and FF = 51.0 %). Moreover, the IDIC16-based PSCs processed by 1,8-diiodooctane (DIO) show a lower PCE of 4.01 % with a dramatically decreased Voc of 0.83 V (Figure S10), which may be due to the over crystallization and strong aggregation of IDIC16 in blends induced by DIO. As shown in Figure 1e, the PF1-TS4-based all-PSC shows a ≈ 30 nm red-shifted external quantum efficiency (EQE) spectrum and higher EQE values in the whole range of 300–785 nm compared to the IDIC16-based PSC. The integrated Jsc values from EQE spectra agree well with the measured ones from J–V plots, with deviations of less than 5 %. The higher PCE of PF1-TS4 in devices implies that the strong benefit of our polymerization strategy by introducing non-conjugated TS4 linkage into polymer backbone.

To understand the photovoltaic performance differences, exciton dissociation probability P(E,T) and charge recombination mechanism were investigated. As shown in Figure S11, the PF1-TS4-based all-PSC shows a higher P(E,T) of 91.1 % than that of 87.8 % for the IDIC16-based PSC under the short-circuit condition, indicating more efficient exciton dissociation and charge extraction,[41] which agree well with its higher Jsc. The relationships between light intensity (P) and Voc, as well as P and Jsc (is defined as Jsc ∝ Pα) were also studied. The PF1-TS4-based all-PSCs show a smaller slope of 1.15 kq/Tq that is closer to 1 in Figure S12 and a higher S value of 0.95 that is closer to 1 in Figure S13 compared to the IDIC16-based PSCs (1.49 kq/Tq and S = 0.91), suggesting less trap-assisted recombination and decreased bimolecular recombination in the PF1-TS4-based device.[41] The improved charge generation and transport properties of the PF1-TS4-based device can be attributed to the fact that the non-conjugated structure of PF1-TS4 increases the miscibility between PF1-TS4 and PM6, thus optimizing blend morphology (discussed right below). Moreover, compared to the PM6 and acceptor neat films, the PM6:PF1-TS4 blends show higher photoluminescence quenching efficiencies of 88.1–91.8 % compared to the PM6:IDIC16 blends (79.5–84.8 %; Figure S14), suggesting better compatibility and more efficient photo-induced charge transfer between PM6 and PF1-TS4 in device.

In GIWAXS measurements (Figure 2), both blend films exhibit favorable π-face-on orientation. The PM6:IDIC6 film has high-order diffraction peaks corresponding to a specific set of (h00) lamellar stacking along the out-of-plane (OOP) direction, indicative of the retained high crystallinity of both two components in blends. Moreover, the overlap of π-π diffractions in PM6:IDIC6 film can be deconvoluted via multiple peaks fitting. The (010) π-face-on stacking crystallite coherence lengths (CCL010) are calculated

![Figure 1](image-url) **Figure 1.** a) Normalized absorption spectra and b) energy level diagrams of PM6, PF1-TS4, and IDIC16 neat films. c) 2D GIWAXS profiles of PF1-TS4 and IDIC16 neat films. d) The J–V plots of the devices under AM 1.5G illumination, 100 mW cm⁻², and e) the corresponding EQE spectra.

355 and 365°C, respectively, compared to IDIC16 (335°C). In differential scanning calorimetry (DSC) analysis (Figure S6), distinct crystallization of two possible phases are pronounced by both heating and cooling thermograms of IDIC6, which indicates strong crystallinity as evidenced by its sharp multi-melting and crystallization peaks. The phase transitions at relatively low temperature of 31 and 44°C imply the poor thermal stability of IDIC6 film and the corresponding blend film when such solar cells are in use. By contrast, PF1-TS4 and PZ1 present no obvious thermal transition, indicating the long polymer chains limit the mobility of the acceptor segments and prevent chain alignment at a broad temperature range of 0–250°C. Therefore, good thermal stability can be expected from such polymer-polymer blends.

Table 1: Photovoltaic data of the devices.

| D:A       | Voc [V] | Jsc [mA cm⁻²][a] | FF [%] | PCE [%][b] |
|-----------|---------|------------------|--------|------------|
| PM6:PF1-TS4 | 0.98    | 15.04 (14.92)    | 58.5   | 8.63 (8.48) |
| PM6:IDIC16 | 0.99    | 11.80 (11.57)    | 51.0   | 5.96 (5.72) |

[a] The integral Jsc in parentheses derived from the EQE curves. [b] The average PCEs in parentheses calculated from 10 devices.
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TS4 blend shows excellent morphological stability under thermal annealing. More meaningfully, the PF1-TS4-based all-PSC still retained \( \approx 70\% \) of its initial PCE after being annealed at 85°C for 180 h, while the IDIC16-based one only retained \( \approx 50\% \) of it when annealed at 85°C for only 18 h. This work clearly demonstrated a new avenue for improving the active layer stability and thus the thermal stability of the resulting devices by developing non-conjugated polymer acceptors, which will inspire not only solar cells community but also the related organic electronics research fields towards practical applications.

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** all-polymer solar cells - non-conjugated polymer acceptors - power conversion efficiency · thermal stability · thioalkyl chain linkages

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An efficient non-conjugated polymer acceptor PF1-TS4 was developed by embedding thioalkyl linkages in the main chain of a conjugated polymer. The resulting all-polymer solar cells achieved a promising device efficiency of 8.63% with excellent thermal stability at 85 °C for 180 hours.