High-Performance Ambient-Condition-Processed Polymer Solar Cells and Organic Thin-Film Transistors

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ABSTRACT: Large-scale commercial synthesis of bulk-heterojunction (BHJ) solar cell materials is very challenging and both time and energy consuming. Synthesis of π-conjugated polymers (CPs) with uniform batch-to-batch molecular weight and low dispersity is a key requirement for better reproducibility of high-efficiency polymer solar cells. Herein, a conjugated polymer (CP) PTB7-Th, well known for its high performance, has been synthesized with high molecular weight and low dispersity in a closed microwave reactor. The microwave reaction procedure is known to be more controlled and consumes less energy. The precursors were strategically reacted for different reaction time durations to obtain the optimum molecular weight. All different CPs were well characterized using 1H NMR, gel permeation chromatography (GPC), UV−vis, photoluminescence (PL), electron spin resonance (ESR), and Raman spectroscopy, whereas the film morphology was extensively studied via atomic force microscopy (AFM) and grazing incidence X-ray diffraction (GIXRD) techniques. The effect of molecular weight on a conventional BHJ solar cell with PC71BM acceptor was investigated to derive systematic structure−property relationships. The CP obtained after 35 min of reaction time and integrated into BHJ devices under ambient conditions provided the best performance with a power conversion efficiency (PCE) of 8.09%, which was quite similar to the results of CPs synthesized via a thermal route. An enhanced PCE of 8.47% was obtained for the optimized polymer (35 min microwave reaction product) when device fabrication was carried out inside a glovebox. The organic thin-film transistor (OTFT) device with the microwave-synthesized CP displayed better hole mobility (0.137 cm² V⁻¹ s⁻¹) as compared to that with the thermally synthesized CP. This study also proved that the device stability and reproducibility of the microwave-synthesized CP were much better and more consistent than those of the thermally developed CP.

INTRODUCTION

Polymer solar cells (PSCs) have gained great attention recently as one of the leading fields within photovoltaic research because of their unique advantages such as light weight, flexibility, easy fabrication, low cost, quick energy payback time, and ease of device fabrication scale-up.1−9 The most established and widely studied device concept among all PSCs is a bulk-heterojunction (BHJ) system, where an acceptor and a donor molecule having complementary optical absorption behavior and well-matched energy levels are blended together to provide a distinct active layer.10 A power conversion efficiency (PCE) of >13% has been reported by designing and developing new molecules and applying different device engineering strategies.11−14

Quite a few molecular designing strategies have been established over the past few years to optimize the optical properties and band gap of donor materials.15 Donor (D)−acceptor (A) copolymerized conjugated polymers (CPs) with low band gaps are widely used as the most successful donors in the active layer of BHJs for improved performance. The optoelectronic properties of the CPs can also be tuned by structure variation of D and A, side chain modulation, and modification of functional groups.15,16 Commonly, these π-conjugated copolymers are synthesized by Pd(Ph₃)₄-catalyzed Stille polycondensation.17 For several D−A CPs, it has been reported that the molecular weight (Mₘ) and polydispersity index (D) of the CPs largely affect the hole mobility, molecular orientation and crystallinity, optoelectronic properties, thin-film morphology, and device performance.18−22 Generally, higher molecular weight CPs demonstrate a better PCE due to enhanced charge carrier mobility, better optical absorption, and superior intermixed film morphology.21−23 Yet, CPs with much higher Mₘ have solubility problems, leading to poor BHJ morphology as well as lower PCE. Recently, it has also been established that with increasing D values of the CPs, the PCE drops gradually.24 Therefore, CPs with optimum Mₘ and lower...
D are needed for better device performances. However, CPs synthesized from metal-catalyzed polycondensation reactions lead to inconsistent device performances from one synthetic batch to another batch. This batch-to-batch variation is due to the differences in \( M_w \), \( M_l \), and residual palladium contamination in various batches.\(^{25-27}\) It is also challenging to synthesize these CPs on a large scale for commercialization. Hence, various methodologies have been carefully investigated for the improvement of the Stille coupling reaction protocol. A recent article has discussed the comparison between CPs achieved from \( \text{Pd}_3(\text{db})_4 \)/P(o-tol)_1\(_2\) and \( \text{Pd}((\text{PPh})_3)_4 \)-catalyzed Stille polycoupling.\(^{28}\) Another report disclosed almost negligible batch-to-batch variations in organic photovoltaic (OPV) performance acquired from stepwise heating in the Stille coupling reaction.\(^{29}\) Nowadays, microwave (MW)-assisted Stille copolymerization is also being used at times to synthesize higher \( M_w \) CPs with lower \( D \).\(^{30,31}\) The MW reactions in a closed (pressurized) reactor is much more advantageous in terms of ultrafast and homogeneous heating and use of a smaller amount of solvent that decrease the side reactions and improve the reaction yields to provide a ultrahigh-quality product. This MW process is also more energy-efficient than conventional heating as well as open-vessel microwave reactions.\(^{32,33}\)

Herein, we present the strategic synthesis of a well-known high-performance donor CP (PTB7-Th) through Stille polycoupling in a closed MW reactor. PTB7-Th CPs with different molecular weights have been synthesized by varying the MW reaction time from 25 to 45 min through single-step heating. All CPs have been characterized by \(^1\)H NMR, gel permeation chromatography (GPC), UV–vis, photoluminescence (PL), Raman, and electron spin resonance (ESR) spectroscopy, atomic force microscopy (AFM), and grazing incidence X-ray diffraction (GIXRD) to reveal the structural differences in terms of \( D-A \) ratios and backbone purity. Conventional BHJ devices (Figure 1a) were fabricated with these MW CPs in combination with PC\(_{71}\)BM, where the active layer was spin-coated under ambient conditions.\(^{34}\) The photovoltaic results of these MW CPs were extensively correlated with the properties of CPs. Multistep heating reactions were also performed, but they resulted in poor device performance and stability. Organic thin-film transistor (OTFT) devices were also fabricated (Figure 1b) with microwave- and thermally synthesized CPs to determine the charge carrier transport behavior of the CPs, where the microwave-synthesized CP showed a better hole mobility of 0.137 cm\(^2\)V\(^{-1}\)s\(^{-1}\).

### RESULTS AND DISCUSSION

**Optical and Electrochemical Characterization.** The optical absorption of the microwave (MW)- and thermally synthesized CPs is depicted in Figure 2a. All CPs exhibit almost similar absorption behavior with a predominant absorption peak at \( \sim 705 \) nm along with an additional peak at \( \sim 635 \) nm. The lower wavelength shoulder peaks appear with equal intensity for MW25m, MW35m, and Thermal CPs, while this is largely increased for the MW45m CP. Moreover, the absorption spectrum becomes more broadened for MW45m compared with those of the other CPs with a blue shift of almost 6 nm (Table 1). These absorption behaviors suggest that MW45m contains higher proportion of homocoupled units, such as \( (4,8\text{-bis}(5\text{-}(2\text{-ethylhexyl})\text{thiophen}-2\text{-yl})\text{-benzo-}[1,2\text{-b}:4,5\text{-b}']\text{dithiophene}-2\text{-,6-diyli)}\text{bis}(\text{trimethylstannane)} \) (BDTT)–BDTT and 2-ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-b][thiophene-2-carboxylate (FTT)–FTT, in the CP backbone.\(^{34,35}\) The optical absorption in blend films (Figure 2b) revealed that the light-harvesting property initially increases with increasing molecular weight but decreases for very high molecular weight. This is because of reduced solubility and deprived film quality of the CP. This can be well correlated with the GPC data (Figures S3–S4). Lower molecular weight CPs (MW25m and MW35m) exhibit unimodal distribution in their molecular weight, whereas MW45m shows a trimodal distribution. This trimodal behavior indicates that the polymer quality is modified in the case of MW45m since the longer time of radiation, although helps to further increase the molecular weight, might lead to the degradation or scission of polymer chains. The electrochemical behavior of the CPs was studied with cyclic voltammetry (see Figure S5).

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of all CPs were also calculated (Table 1). MW45m exhibits a lower lying HOMO as compared to other CPs (Figure S6).

The backbone irregularities of the CPs were well examined by Raman spectroscopy (Figure 2c). The vibrational modes of thiophenes, existing in the CPs, are Raman-active because of their prominent coupling with the delocalized \( \pi \)-electrons. All CPs disclose five significant Raman peaks.\(^{28}\) Thermal, MW25m, and MW35m exhibit similar spectra, whereas MW45m shows a significant change in Raman vibrational modes. The coupled vibration of the stretching mode (\( C=C \)) of fused thiophenes (present in the BDTT unit) to the non-fluorinated thiophenes of the FTT unit (peak 3) and the coupled vibration of the stretching mode (\( C=C \)) of the non-fluorinated thiophene to the quadrant stretching mode (peak 4) of MW45m illustrate a much broader and higher intensity spectrum. Also, stretching modes (\( C=C \)) of the side chain thiophenes in the BDTT unit (peak 1) of this CP are observed with a higher intensity along with a shift of \( \sim 3 \) cm\(^{-1}\) to higher wavenumbers. This enhanced intensity of the vibrational modes in the Raman spectrum is evidence for the presence of homocoupled units in the CP main chain. Hence, Thermal, MW25m, and MW35m have a much lower quantity of defective units as compared to MW45m. These defective units in the CP backbone can act as deep traps in photovoltaic devices and might hamper device performance. Photo-luminescence (PL) study (Figure 2d) was performed to estimate the emission strength of the CPs having different molecular weights. MW35m has an improved emission compared with MW25m due to its higher molecular weight. The Thermal CP also reveals slightly lower emission in comparison to MW35m. However, MW45m shows a lower emission in spite of having a higher molecular weight. This can
be described by considering the structural defects and, hence, self-quenching caused by photoinduced charge transfer from the regular repeating units of the CP to the homocoupled defect units.

**ESR Spectroscopy.** Considering the information about the synthesis and physical characteristics of the synthesized CPs, it can be assumed that the molecular framework of the CPs does not introduce any spin-active species. Therefore, the ESR spectra of the studied CPs should not display any type of ESR signal. Nevertheless, they reveal a prominent ESR signal, which evidences the existence of radical species (Figure 3). It is believed that the presence of ESR signal is due to some structural defects of the CP backbone or some unpaired electrons coming from chemical impurities. These radical species may act as deep traps for mobile charge carriers and greatly affect the solar cell device performance of the CP.\(^{36}\) ESR spectra of all CPs showed a similar polycrystalline pattern with a \(g\) factor of 1.998 ± 0.001. The signal intensity is proportional to the concentration of radical species. MW25m and MW35m demonstrate almost comparable signal intensity, which implies equivalent radical concentration. The Thermal CP shows a higher signal intensity in comparison to MW35m. However, MW45m has a much higher radical concentration as indicated by its enhanced signal intensity. Hence, MW45m has more trap states than MW25m and MW35m, which could hinder the charge transport in the solar cell device. From this result, we can expect that the MW45m CP will give a lower photocurrent \(J_{sc}\) and mobility.

**Solar Cell Device Characterization.** OPV devices with a conventional architecture were fabricated for the assessment of photovoltaic properties of the donor CP along with PC\(_{71}\)BM as the acceptor. During device fabrication, the active layer was

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![Figure 2](https://example.com/figure2.png)

**Figure 2.** UV−vis absorption spectra of (a) CP thin films, (b) polymer−PC\(_{71}\)BM blend thin films, (c) Raman spectra under 514 nm excitation, and (d) PL spectra of CP thin films.

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![Figure 3](https://example.com/figure3.png)

**Figure 3.** X-band RT dark ESR spectra of MW25m, MW35m, and MW45m powders.

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![Table 1](https://example.com/table1.png)

**Table 1. Molecular Weight, Optical Properties, and Electronic Energy Levels of the Synthesized Polymers**

| polymer  | \(M_n\) (kDa) | \(M_w\) (kDa) | PDI | \(\lambda_{\text{max}}\) film (nm) | \(\lambda_{\text{edge}}\) film (nm) | \(E_g\) optical (eV) | HOMO (eV) | LUMO (eV) |
|---------|---------------|---------------|-----|---------------------------------|-------------------------------|-----------------|-----------|-----------|
| MW25m   | 27.6          | 64.1          | 2.32 | 706                            | 772                          | 1.60            | -5.31     | -3.71     |
| MW35m   | 63.1          | 167.2         | 2.65 | 708                            | 784                          | 1.58            | -5.32     | -3.74     |
| MW45m   | 66.9          | 202.3         | 3.02 | 701                            | 779                          | 1.59            | -5.39     | -3.80     |
| Thermal | 49.5          | 149.3         | 3.01 | 706                            | 779                          | 1.59            | -5.29     | -3.70     |
spin-coated under ambient conditions (outside the glovebox in the presence of air). The current density–voltage (J–V) characteristics of the air-processed devices for the four CPs are shown in Figure 4a (the data are summarized in Table 2). The data indicate that with increasing molecular weight of the CPs (from 64.1 to 167.2 kDa) the PCE is enhanced significantly from 5.97 to 8.09%. However, a further increase in molecular weight results in a reduction of the PCE. A comparable trend from 5.97 to 8.09%. However, a further increase in molecular weight is essential for better solar cell performance. Therefore, an optimal molecular weight is essential for better solar cell performance. Moreover, the CPs synthesized from different batches of microwave reaction show outstanding reproducibility by suppressing the batch-to-batch variation in solar cell device performance (Figure S8). To further increase the device performance of the optimized CP, MW35m, devices are fabricated inside a glovebox to observe an enhanced PCE of 8.47% (Table S2 and Figure S9).

External quantum efficiency (EQE) spectra of all solar cell devices demonstrate a strong photoresponse in the broad spectral region from 300 to 800 nm (Figure 4b). The considerable variations of the \( J_{sc} \) values, obtained from J–V measurements, are well reflected in their EQE spectra. The integrated \( J_{sc} \) values calculated from EQE spectra are 14.27, 11.81, 14.36, and 6.95 mA cm\(^{-2}\) for Thermal, MW25m, MW35m, and MW45m, respectively, with a discrepancy of \( \sim 7\% \) compared to the \( J_{sc} \) values obtained from the J–V curve. This mismatch may be attributed to the different measurement conditions. The J–V characterization was carried out inside a glovebox under an argon atmosphere, whereas the EQE measurements were executed outside the glovebox.

### OTFT Device Characterization

OTFT devices with top-contact/bottom-gate geometry were fabricated with MW35m and Thermal CPs to evaluate the charge transport in two CPs. The devices were fabricated under ambient conditions with two organic dielectric layers (poly(vinyl alcohol) (PVA) and poly(methyl methacrylate) (PMMA)) and CPs as the active layer. The OTFT device parameters are presented in Table 3, and the output and transfer characteristics are shown in Figure 5. The device with the Thermal CP shows a current on/off ratio of \( 6 \times 10^4 \) and a high hole mobility of 0.024 cm\(^2\) V\(^{-1}\) s\(^{-1}\) in the linear region, whereas MW35m demonstrates a better device performance with a higher hole mobility of 0.137 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and a current on/off ratio of \( 2 \times 10^4 \). Both the CPs exhibit almost similar root-mean-square (rms) roughness of \( \sim 1.1 \) nm in the AFM study (Figure S10). Therefore, the higher hole mobility and lower off-current of MW35m in comparison to those of the Thermal CP can explain its enhanced emission intensity. Also, MW35m exhibits a lower ESR signal intensity, which implies lower radical concentration and lower trap density.

### Morphological Characterization

The morphology of the blend films was extensively studied by atomic force microscopy (AFM) to reveal the effect of molecular weight of the MW-synthesized CPs (Figure 6a–d). The topographic images of the blend films did not display any difference in

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**Table 2. Photovoltaic Parameters of PSCs under Standard AM1.5G Illumination**

| Device      | \( J_{sc} \) (mA cm\(^{-2}\)) | \( V_{oc} \) (V) | FF  | max. PCE (ave. PCE, %) |
|-------------|--------------------------------|-----------------|-----|------------------------|
| MW25m       | 11.97                          | 0.819           | 0.61| 5.97 (5.54 ± 0.33)      |
| MW35m       | 15.30                          | 0.826           | 0.64| 8.09 (7.53 ± 0.33)      |
| MW45m       | 7.24                           | 0.858           | 0.50| 3.12 (2.61 ± 0.34)      |
| Thermal     | 15.27                          | 0.817           | 0.63| 7.91 (7.27 ± 0.47)      |

*Average PCE of 10 devices. Average PCE of 30 devices.*

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**Table 3. Device Parameters of OTFTs**

| Device      | Mobility (cm\(^2\) V\(^{-1}\) s\(^{-1}\)) (ave. mobility) | \( V_{th} \) (V) | \( L_{on}/L_{off} \) |
|-------------|----------------------------------------------------------|-----------------|---------------------|
| MW35m       | 0.137 (0.110)                                            | 19.5            | \( 2 \times 10^4 \) |
| Thermal     | 0.024 (0.019)                                            | 22              | \( 6 \times 10^2 \) |

*Average of three devices.*
microstructures with a comparable rms roughness of ∼1.4 nm for all films. Therefore, the morphology of the donor−acceptor blends was evaluated through a grazing incidence X-ray diffraction (GIXRD) study to obtain clear insight into the crystallinity and molecular packing of different films. The (100) lamellar peaks are observed in the in-plane profile at $q_{xy}$ = 2.78, 2.71, 2.86, and 2.64 nm$^{-1}$ and the calculated lamellar spacings are 2.26, 2.32, 2.20, and 2.38 nm for blends of Thermal, MW25m, MW35m, and MW45m, respectively (Figure S11 and Table S3). Hence, MW45m exhibits the

Figure 5. (a, c) Typical output curves and (b, d) transfer plots of the bottom-gate/top-contact OFET devices using MW35m and Thermal CPs, respectively.

Figure 6. AFM images of donor−acceptor blends for (a) MW25m, (b) MW35m, (c) MW45m, and (d) Thermal; 2D GIWAX images of donor−acceptor blends for (e) MW25m, (f) MW35m, (g) MW45m, and (h) Thermal.
highest lamellar spacing among all, and hence, transport of charge becomes difficult. Similarly, the \( \pi-\pi \) stacking peaks are calculated from the one-dimensional (1D) line-cut profile obtained at \( q_z = 13.31, 13.31, 13.31, \) and \( 13.46 \text{ nm}^{-1} \) for blends of Thermal, MW25m, MW35m, and MW45m, respectively, and the calculated \( \pi-\pi \) stacking is \( \sim 0.47 \) nm. The lamellar peak intensity of MW35m is much higher in comparison to those of other CPs in the in-plane and out-of-plane directions. A similar trend is also observed for the \( \pi-\pi \) stacking peak intensity. These data indicate that MW35m exhibits a more preferential face-on orientation than other CPs. The face-on orientation in the donor–acceptor blend is favorable for better vertical charge transport, which improves the PSC performance. Figure 6e–h shows the two-dimensional (2D) \( q \)-plot of the blend films of the three samples. All four blends show unique characteristics of concentric circles in their films. No prominent concentric circles are found in any of the samples. But looking at the 2D \( q \)-plot, it can be confirmed that the film of the MW35m blend is the most crystalline having one discrete circle and the film of the MW45m blend is found to be the most amorphous having diffused circles in the 2D \( q \)-plot. The crystallinity of the film of Thermal and MW25m blends is in between those of the MW35m and MW45m samples. This result can be well compared with the device result, i.e., the MW35m blend displays the highest PCE (also the result can be well compared with the device result, i.e., the MW35m blend displays the highest PCE). This study is also observed for the \( \pi-\pi \) stacking peak intensity. This can be well compared with the device result, i.e., the MW35m blend displays the highest PCE (also the result can be well compared with the device result, i.e., the MW35m blend displays the highest PCE).

**Stability Study.** Stability is a very important parameter for any type of solar cell for real-life applications. The thermal stability of the best device was studied for unencapsulated devices stored in an argon atmosphere. For this study, the device was heated at \( 70 \, ^\circ\text{C} \) and thermally synthesized PTB7-Th devices were taken as controls. It could be clearly seen that the MW-synthesized CP showed better thermal stability compared to the Thermal CP (Figure 7). Both the CPs revealed a sharp decay in their PCE within the first 250 min. After that, the efficiency of MW35m entered into a stable zone and remained almost unchanged, whereas for Thermal, the PCE kept on decreasing. After 1500 min of heating, MW35m degraded up to 56% but Thermal retained only 16% of its original PCE. A comparison of the device efficiency and stability achieved in this work with those in recent reports is given in Table S4. This illustrates that the microwave reaction method is a very promising technology for the development of high-performance and stable solar cells.

**CONCLUSIONS**

In this work, controlled synthesis of PTB7-Th in a closed-vessel microwave reactor has been successfully achieved. This reaction protocol is very convenient to synthesize CPs with higher \( M_w \) and comparatively lower \( D \), consuming much lower energy. Importantly, this method offers much better quality materials for devices with very low batch-to-batch variation, which is very important for large-scale commercial synthesis of donor CPs through Stille polycondensation. As a remarkable development, the device fabrication was carried out under ambient conditions unlike most cases, where a purely inert atmosphere is followed. MW35m (with a higher \( M_w \) of 167.2 kDa and a lower \( D \) value of 2.67) shows an efficiency of 8.09%, with a FF of 64%, a \( V_{OC} \) of 0.826 V, and a \( J_{SC} \) of 15.30 mA cm\(^{-2}\), which is very consistent and better than that of the CP synthesized through a thermal route, and the PCE is further improved to \( \sim 8.5\% \) in devices fabricated inside the glovebox. These PCE values are among the highest efficiency for PTB7-Th in air/ambient-processed and inert-condition devices. Additionally, the OTFT devices fabricated using MW35m exhibit a better hole mobility of 0.137 cm\(^2\) V\(^{-1}\) s\(^{-1}\).

**EXPERIMENTAL SECTION**

**Materials and Methods.** The monomers, 2-ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-b]thiophene-2-carboxylate [FTT] and (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) [BDTT], were obtained from Derthon Optoelectronic Materials Science Technology Co. Ltd. and directly used. Indium tin oxide (ITO) substrates (15 Ω sq\(^{-1}\)) and poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) (PVP AI4083) was received. Materials and Methods. The monomers, 2-ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-b]thiophene-2-carboxylate [FTT] and (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) [BDTT], were obtained from Derthon Optoelectronic Materials Science Technology Co. Ltd. and directly used. Indium tin oxide (ITO) substrates (15 Ω sq\(^{-1}\)) and poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) (PVP AI4083) was received. All other chemicals were used as received.

**Synthesis and Characterization of CPs.** Monomers BDTT (100 mg, 0.11 mmol) and FTT (52 mg, 0.11 mmol) were introduced into the microwave reactor vessel (closed). A solvent mixture of toluene–dimethylformamide (DMF) (3:1, 2 mL) was added to it. After that, argon was purged for 20 min; the Pd(PPh\(_3\))\(_4\) catalyst was then added to the reaction mixture and again argon was purged for 20 min. Finally, the reactor vessel was refluxed at 150 °C under microwave conditions (microwave power 150 W and pressure 20 psi) for different time durations (25, 30, 35, 40, and 45 min) strategically to prepare CPs with varying molecular weights. After completion, the resulting CP solution was precipitated in 200 mL of methanol. The precipitate was then further purified through Soxhlet extraction sequentially with 300 mL each of methanol, hexane, acetone, and chloroform. Again the solution was passed through a Celite bed. The CP was further precipitated in methanol and finally the pure CP was dried in a vacuum. This CP was also synthesized by a conventional process. The CP was also synthesized by a conventional process. The CP was also synthesized by a conventional process. The CP was also synthesized by a conventional process.
MW45sm: (yield 56%) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.18−7.84 (br, 5H), 6.56−6.99 (br, 2H), 4.06−4.59 (br, 2H), 2.63−3.29 (br, 4H), 0.72−1.95 (br, 46H).

Thermal: (yield 54%) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.23−7.69 (br, 5H), 6.69−7.04 (br, 2H), 4.07−4.59 (br, 2H), 2.65−3.27 (br, 4H), 0.67−1.96 (br, 46H).

**Device Fabrication. Solar Cells.** PSC devices were fabricated with the conventional architecture of ITO/PEDOT:PSS/donor polymer:PC$_{71}$BM/Ca/Al. Each device had a cell area of 0.06 cm$^2$. The donor−acceptor blend solution (for the active layer) was prepared using chlorobenzene (CB) as a processing solvent at a concentration of 35 mg mL$^{-1}$ (D/A ratio 1:1.5). Then, it was kept at 50 °C and constantly stirred for 6 h for proper dissolution, and a small amount (3%, volume) of 1,8-diiodooctane (DIO) was also added to it 15 min before spin coating. Patterned ITO glass substrates were cleaned sequentially using deionized (DI) water, acetone, and isopropanol. Then, they were dried using dry N$_2$ gas, and UV−ozone treatment was carried out for 20 min. Next, PEDOT:PSS (Al4083) was spin-coated on the ITO substrate at 4000 rpm and then annealed at 140 °C for 10 min. After cooling, the blend solution was spin-coated at 3000 rpm followed by methanol treatment for the removal of DIO. Lastly, calcium (~20 nm) and aluminum (~100 nm) were thermally deposited (ca. 5 × 10$^{-6}$ Pa) onto the MeOH-treated active layer. Except for metal deposition, the entire device was fabricated under ambient conditions.

**OTFT.** OTFTs were fabricated on glass substrates. An aluminum gate electrode of thickness 100 nm (width 1 mm) was thermally deposited on the glass substrate using a shadow mask. On it, 10% w/v PVA solution in DI water was spin-coated at 3000 rpm for 60 s and annealed for 30 min at 100 °C to give a layer of 1 μm thickness. Then 3% w/v PMMA solution in anisole was spin-coated at 3000 rpm for 60 s and annealing was performed at 100 °C for 90 min. The thickness of the PMMA layer was determined to be 100 nm. The CP solution (10 mg mL$^{-1}$) in CB was used as the active layer, and 1% DIO was added to it 15 min before coating. The polymeric active layer was spin-coated on the PMMA surface at 2000 rpm for 60 s and then annealed at 70 °C for 10 min. All device fabrication procedures were carried out under ambient conditions. For source−drain electrodes, a buffer layer of ∼5 nm MoO$_3$ and ∼60 nm copper was thermally deposited. The devices were fabricated with a channel length ($L$) of 40 μm and channel width ($W$) of 800 μm through a shadow mask.

**REFERENCES**

(1) Heeger, A. J. 25th Anniversary Article: Bulk Heterojunction Solar Cells: Understanding the Mechanism of Operation. *Adv. Mater.* 2014, 26, 10−28.

(2) Lu, L.; Zheng, T.; Wu, Q.; Schneider, A. M.; Zhao, D.; Yu, L. Recent Advances in Bulk Heterojunction Polymer Solar Cells. *Chem. Rev.* 2015, 115, 12666−12731.

(3) Krebs, F. C.; Gevorgyan, S. A.; Alstrup, J. A Roll-to-Roll Process to Flexible Polymer Solar Cells: Model Studies, Manufacture and Operational Stability Studies. *J. Mater. Chem.* 2009, 19, 5442−5451.

(4) Li, Y. Molecular Design of Photovoltaic Materials for Polymer Solar Cells: Toward Suitable Electronic Energy Levels and Broad Absorption. *Acc. Chem. Res.* 2012, 45, 723−733.

(5) Kang, H.; Kim, G.; Kim, J.; Kwon, S.; Kim, H.; Lee, K. Bulk-Heterojunction Organic Solar Cells: Five Core Technologies for Their Commercialization. *Adv. Mater.* 2016, 28, 7821−7861.

(6) Polman, A.; Knight, M.; Garnett, E. C.; Ehlers, B.; Sinke, W. C. Photovoltaic Materials: Present Efficiencies and Future Challenges. *Science* 2016, 352, No. 6242.

(7) Chen, C.-C.; Dou, L.; Zhu, R.; Chung, C.-H.; Song, T.-B.; Zheng, Y. B.; Hawks, S.; Li, G.; Weiss, P. S.; Yang, Y. Visibly Transparent Polymer Solar Cells Produced by Solution Processing. *ACS Nano* 2012, 6, 7185−7190.

(8) Peters, C. H.; Sachs-Quintana, I. T.; Kastrop, J. P.; Beaupré, S.; Leclerc, M.; McGhee, M. D. High Efficiency Polymer Solar Cells with Long Operating Lifetimes. *Adv. Energy Mater.* 2011, 1, 491−494.

(9) Darling, S. B.; You, F. The Case for Organic Photovoltaics. *RSC Adv.* 2013, 3, 17633−17648.

(10) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions. *Science* 1995, 270, 1789−1791.
Molecular Optimization Enables over 13% Efficiency in Organic Solar Cells. J. Am. Chem. Soc. 2017, 139, 7148−7151.

Zhao, W.; Li, S.; Yao, H.; Zhang, S.; Zhang, Y.; Yang, B.; Hou, J. Ternary Polymer Solar Cells Based on Two Acceptors and One Donor for Achieving 12.2% Efficiency. Adv. Mater. 2017, 29, No. 1604059.

Li, M.; Gao, K.; Pan, X.; Zhang, Q.; Kan, B.; Xia, R.; Liu, F.; Yang, X.; Feng, H.; Ni, W.; et al. Solution-Processed Organic Tandem Solar Cells with Power Conversion Efficiencies >12%. Nat. Photonics 2017, 11, 85−90.

Zhong, Z.-G.; Qi, B.; Jin, Z.; Chi, D.; Qi, Z.; Li, Y.; Wang, J. Perylene Diamides: A Thickness-Insensitive Cathode Interlayer for High Performance Polymer Solar Cells. Energy Environ. Sci. 2014, 7, 1966−1973.

Yao, H.; Ye, L.; Zhang, H.; Li, S.; Zhang, S.; Hou, J. Molecular Design of Benzodithiophene-Based Organic Photovoltaic Materials. Chem. Rev. 2016, 116, 7397−7457.

Narasimhan Arunagirinathan, R.; Gopikrishna, P.; Das, D.; Iyer, P. K. Solution Processed Donor-Acceptor Polymer Based Electrical Memory Device with High On/Off Ratio and Tunable Properties. ACS Appl. Electron. Mater. 2019, 1, 600−607.

Carsten, B.; He, F.; Son, H. J.; Hu, T.; Yu, L. Stille Polycoupling for Synthesis of Functional Materials. Chem. Rev. 2011, 111, 1493−1528.

Osaka, I.; Saito, M.; Mori, H.; Koganezawa, T.; Takimiya, K. Drastic Change of Molecular Orientation in a Thiazolothiazole Copolymer by Molecular-Weight Control and Blending with PC 61 BM Leads to High Efficiencies in Solar Cells. Adv. Mater. 2012, 24, 425−430.

Li, W.; Yang, L.; Tumbleston, J. R.; Yan, L.; Ade, H.; You, W. Controlling Molecular Weight of a High Efficiency Donor-Acceptor Conjugated Polymer and Understanding Its Significant Impact on Photovoltaic Properties. Adv. Mater. 2014, 26, 4456−4462.

Li, Z.; Yang, D.; Zhao, X.; Zhang, J.; Zhang, J.; Yang, X. Achieving an Efficiency Exceeding 10% for Fullerene-Based Polymer Solar Cells Employing a Thick Active Layer via Tuning Molecular Weight. Adv. Funct. Mater. 2018, 28, No. 1705257.

Liu, C.; Wang, K.; Hu, X.; Yang, Y.; Hsu, C.; Zhang, W.; Xiao, S.; Gong, X.; Cao, Y. Molecular Weight Effect on the Efficiency of Polymer Solar Cells. ACS Appl. Mater. Interfaces 2013, 5, 12163−12167.

Hoefler, S. F.; Rath, T.; Pastukhova, N.; Pavlica, E.; Scheunemann, D.; Wilken, S.; Kunert, B.; Resel, R.; Hobisch, M.; Xiao, S.; et al. The Effect of Polymer Molecular Weight on the Performance of PTB7-Th:O-IDTBR Non-Fullerene Organic Solar Cells. J. Mater. Chem. A 2018, 6, 9506−9516.

Kang, H.; Uddin, M. A.; Lee, C.; Kim, K.-H.; Nguyen, T. L.; Lee, W.; Li, Y.; Wang, C.; Woo, H. Y.; Kim, B. J. Determining the Role of Polymer Molecular Weight for High-Performance All-Polymer Solar Cells: Its Effect on Polymer Aggregation and Phase Separation. J. Am. Chem. Soc. 2015, 137, 2359−2365.

Lu, L.; Zheng, T.; Xu, T.; Zhao, D.; Yu, L. Mechanistic Studies of Effect of Dispersity on the Photovoltaic Performance of PTB7 Polymer Solar Cells. Chem. Mater. 2015, 27, 537−543.

Bartelt, J. A.; Douglas, J. D.; Mateker, W. R.; Labban, A. E.; Tassone, C. J.; Toney, M. F.; Fréchet, J. M. J.; Beaupre, P. M.; McGehee, M. D. Controlling Solution-Phase Polymer Aggregation with Molecular Weight and Solvent Additives to Optimize Polymer-Fullerene Bulk Heterojunction Solar Cells. Adv. Energy Mater. 2014, 4, No. 1301733.

Horns, R. C.; de Bettignies, R.; Leroy, J.; Baillif, S.; Firon, M.; Sentenac, C.; Khourk, A.; Puechhomme, H.; Dagon-Lartigau, C. High Molecular Weights, Polydispersities, and Annealing Temperatures in the Optimization of Bulk-Heterojunction Photovoltaic Cells Based on Poly-3-Thiophene) or Poly-(3-Butylthiophene). Adv. Funct. Mater. 2006, 16, 2263−2273.

Nikiforov, M. P.; Lai, B.; Chen, W.; Chen, S.; Schaller, R. D.; Strzalka, J.; Maser, J.; Darling, S. B. Detection and Role of Trace Impurities in High-Performance Organic Solar Cells. Energy Environ. Sci. 2013, 6, 1513.

Gao, J.; Wang, W.; Zhang, S.; Xiao, S.; Zhan, C.; Yang, M.; Lu, X.; You, W. Distinction between PTB7-Th Samples Prepared from Poly(3-Hexylthiophene) or Poly(3-Butylthiophene). Adv. Funct. Mater. 2006, 16, 2263−2273.