

Double-Cable Conjugated Polymers with Fullerene Pendant for Single-Component Organic Solar Cells

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Electronic Supplementary Information

Abstract In this work, the “functionalization-polymerization” (FP) method has been used to construct fullerene-contained double-cable conjugated polymers with “donor-acceptor” backbones. It was realized via synthesizing a fullerene-contained monomer and performing Stille polymerization. With this method, a series of double-cable conjugated polymers with different fullerene contents were developed and applied into single-component organic solar cells. The power conversion efficiencies (PCEs) based on these polymers increased from 0.71% to 1.71% with the enhanced fullerene contents. The relatively low PCEs might be originated from the poor microstructure in these polymers. These new conjugated polymers with molecular heterojunction would show potential application in organic electronic devices.

Keywords Double-cable conjugated polymers; Single-component organic solar cells; Fullerene; “Donor-acceptor” conjugated polymers; Microphase separation

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INTRODUCTION

Conjugated polymers used for organic solar cells (OSCs) mainly contain homopolymers (such as poly(3-hexyl)thiophene, P3HT),^[1] alternative copolymers with “donor-acceptor” structures,^[2,3] random copolymers,^[4–8] diblock copolymers^[9–16] and double-cable polymers.^[17–25] Among them, diblock copolymers and double-cable polymers contain electron-donor and electron-acceptor in a single polymer chain to facilitate charge separation and transport, so that they can be applied into single-component organic solar cells (SCOSCs).^[17,26,27] In recent years, SCOSCs based on double-cable conjugated polymers and diblock copolymers have obtained rapid progress with power conversion efficiencies (PCEs) over 8%^[18,28–35] and 10%^[7,36] due to the development of new polymer materials.^[37] Additionally, these cells exhibit super thermal, light, and bending stability in rigid and flexible devices, indicating their great potential application.^[38,39]

Double-cable conjugated polymers were firstly reported in

1996, in which the fullerene-pendent monomer was synthesized and electrochemical polymerization was then performed to generate polymers.^[40] This polymerized method was then used to construct double-cable polymers, but its difficulty to control the polymerization and the side reaction limited its application.^[41–43] In 2001, Janssen *et al.* and Inganäs *et al.* constructed fullerene-based monomers to perform polymerization via Sonagashira or FeCl₃-catalyzed oxide reaction, so that polythiophene (PT) and poly(vinylene) based double-cable conjugated polymers were obtained.^[44,45] This is also called the “functionalization-polymerization” (FP) method. For comparison, the “polymerization-post functionalization” (PPF) was then a popular method to construct double-cable conjugated polymers, in which conjugated polymers were synthesized and then fullerene derivatives were introduced into side chains via click reaction.^[20,23–25] Since 2017, we used the FP method to construct double-cable conjugated polymers, in which rylene diimides-based electron acceptors were attached to the side chains of monomers for Stille polymerization.^[18] The FP method enables double-cable conjugated polymers to have tunable physical and optoelectrical properties, so as to enhance the PCEs in SCOSCs.

Fullerene derivatives as well-known electron acceptors have been incorporated into double-cable conjugated polymers, but most of them used P3HT as conjugated backbone via PPF method.^[17,22] It will be interesting to develop func-

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tionalized monomers with fullerene pendant to construct double-cable conjugated polymers *via* the FP method. Herein, we developed a benzodithiophene (BDT) monomer containing a fullerene side unit (**M1**), which was used for Stille polymerization by using a bisstannyl-benzodithiophene-4,8-dione (**M3**). A series of double-cable conjugated polymers **P1–P4** with different contents of fullerene side units were obtained (Scheme 1), in which the physical properties of these new polymers were studied and SCOSCs based on them as photoactive layers were then fabricated to provide PCEs up to 1.71%.

EXPERIMENTAL

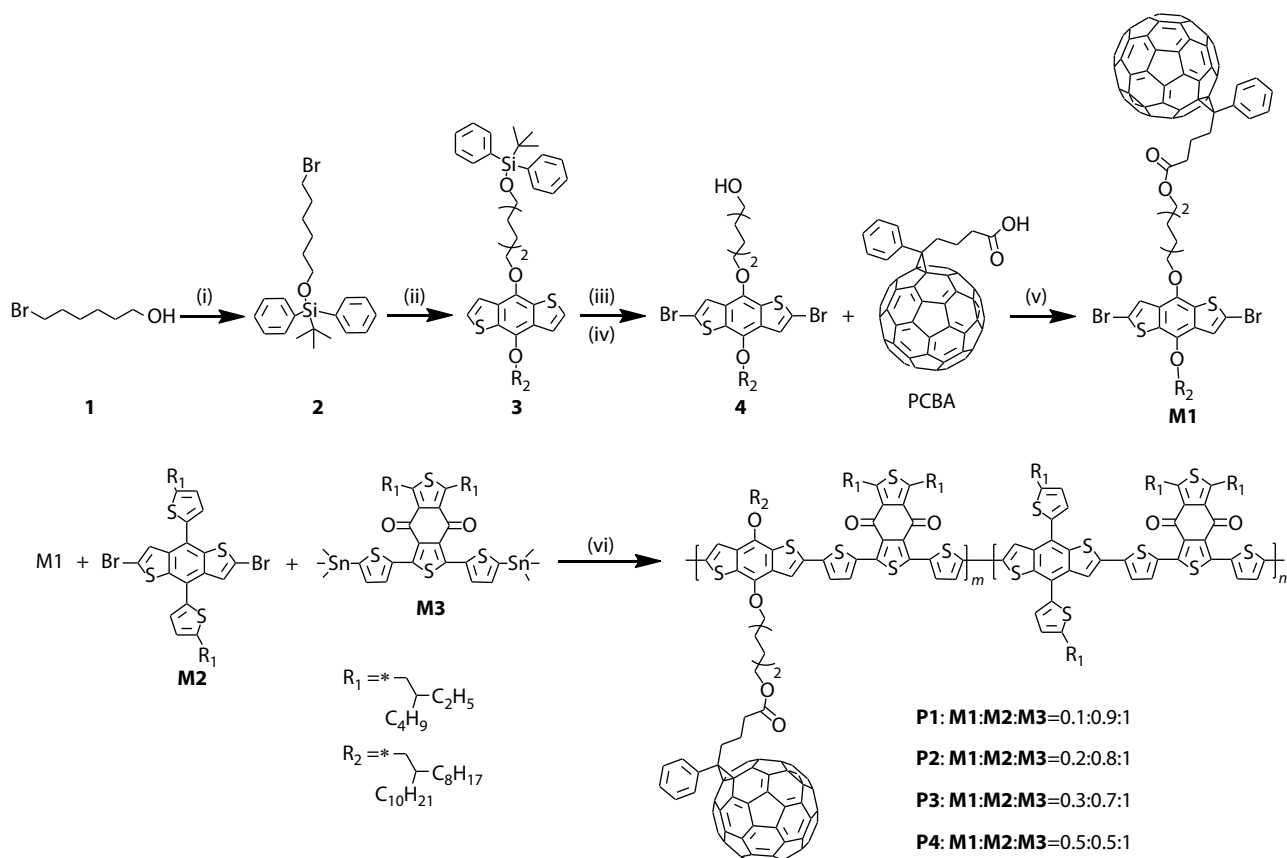
The detailed description of material synthesis is shown in electronic supplementary information (ESI).

RESULTS AND DISCUSSION

The synthetic routes for the key monomer **M1** and the polymers were present in Scheme 1. The detailed procedures were described in ESI. OH group of the starting compound **1** was protected to yield compound **2**, and then was used to synthesize the asymmetric compounds **3** and **4**. The monomer **M1** was obtained *via* condensation reaction by using compound **4** and PC₆₁BA (fullerene phenyl[C₆₁]butyric acid).

Initially, we attempted to use the monomers **M1** and **M3** to construct conjugated polymers, but the resulting polymer was completely insoluble in traditional solvents. This was a surprising result since we used long branched alky side units in **M1** and **M3**, which may be explained by the strong aggregation of fullerene units in the polymer. Therefore, we introduced another monomer **M2** (Scheme 1) to dilute the content of fullerene side units, yielding double-cable conjugated polymers **P1–P4** with the distinct feeding ratios of **M1:M2** (0.1:0.9, 0.2:0.8, 0.3:0.7 and 0.5:0.5) (Scheme 1). All these polymers were readily dissolved in chlorobenzene (CB) that can be solution-processed to fabricate photovoltaic devices.

The molecular weight of the polymers was determined by high-temperature gel permeation chromatography (GPC) measurement by using 1,2,4-trichlorobenzene as the eluent under 150 °C, as summarized in Table S1 (in ESI). **P1** exhibited a number-average molecular weight (M_n) of 23.2 kDa and a polydispersity (M_w/M_n) of 1.64. **P2** and **P3** show the similar M_n with **P1**, while M_n of **P4** is reduced (11.3 kDa) compared to **P1–P3**. This is due to the poor solubility of **P4** with enhanced fullerene content, in which precipitation of **P4** could be observed during polymerization. The thermal stability was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The decomposition temperatures (5% weight loss) of these polymers are all above 370 °C, demon-



Scheme 1 The chemical structures of the fullerene-based double-cable conjugated polymers and their synthetic routes: (i) *tert*-butyldiphenylchlorosilane (TBDPSCI), TEA, DMAP, CH₂Cl₂; (ii) 4,8-dihydrobenzo[1,2-b:4,5-b']dithiophene-4,8-dione, 9-(bromomethyl)nonadecane, tetrabutylammonium bromide (TBAB), NaOH(aq.); (iv) tetrabutylammonium fluoride (TBAF), THF, 0 °C; (v) PC₆₁BA, DMAP, EDCl, *o*-DCB; (vi) Stille polymerization *via* toluene, Pd(PPh₃)₂Cl₂ under 115 °C.

strating excellent thermal stability (Fig. S1 in ESI). Meanwhile, the decomposition temperatures decrease with the fullerene contents increasing, which may be due to the lower molecular weight and is consistent with the literature.^[46] From DSC measurement, no phase transition was observed (Fig. S2 in ESI), which is different from imide-based double-cable conjugated polymers.^[29,32]

It is important to confirm the fullerene content on these polymers, which was studied by nuclear magnetic resonance (NMR) spectra, as shown in Fig. 1. The denoted H protons in the red rectangular of the NMR spectra are assigned as $-\text{CH}_2\text{OR}$ from the monomer **M1** with fullerene pendant. When increasing the content ratio of **M1** for Stille polymerization, their peak intensity was enhanced, which can confirm the enhancement of fullerene content in the polymer **P1–P4**. Furthermore, the denoted H protons in the blue rectangular

of the NMR spectra are assigned as $-\text{CH}_2\text{R}$ attached to BDD units. The detailed NMR spectra and the integration are present in ESI. Therefore, we are able to use these two typical peaks to estimate the loading amount of fullerene, in which the ratio of m:n is 1:2.2, 1:1.5, 1:1 and 1.6:1 for **P1–P4**, respectively. Considering the feed ratios of **M1:M2** in these polymers, the polymers contain high content of fullerene units, indicating that **M1** with fullerene side unit has higher reactivity than that of **M2** during Stille polymerization.

The absorption spectra of **P1–P4** in solution and thin films are shown in Figs. 2(a) and 2(b). The absorption intensity in the range of 300–400 nm was enhanced from **P1** to **P4** due to the increased content of fullerene side units. **P1–P3** exhibited broad absorption spectra in the range of 500–700 nm due to the conjugated backbone. **P4** had the different spectra in solution with a shoulder at ~650 nm, which

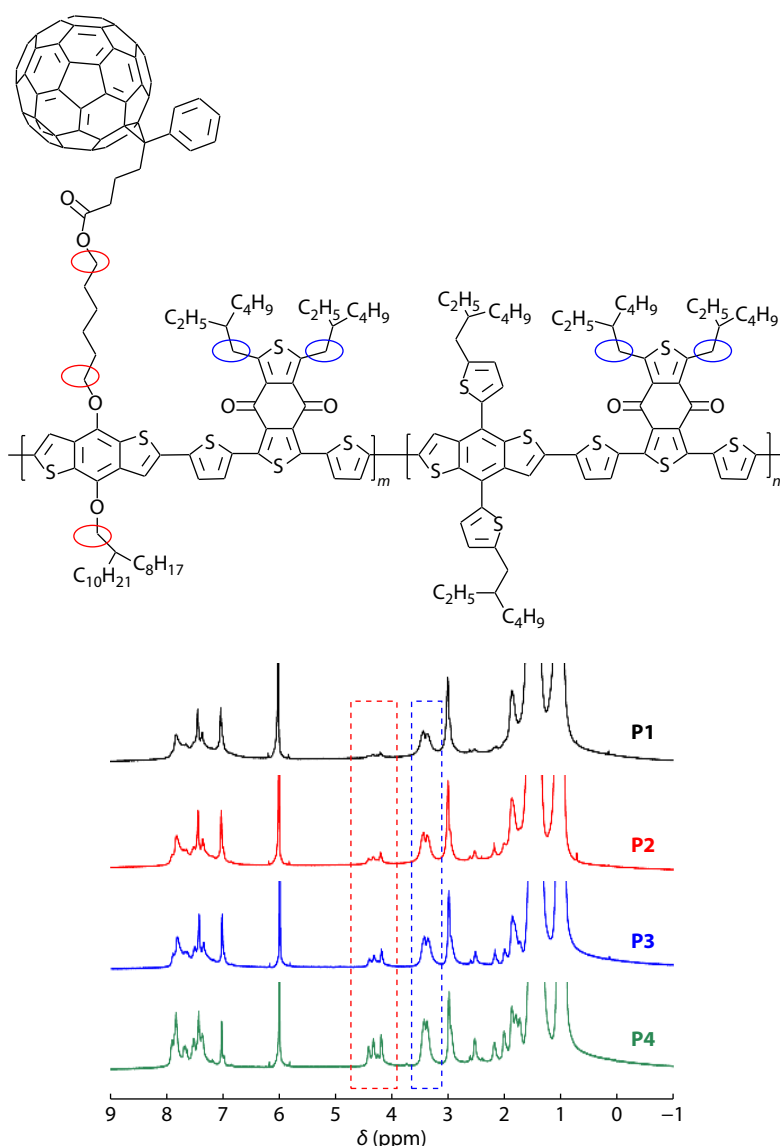


Fig. 1 ^1H -NMR spectra of the polymers **P1–P4** recorded at 100 °C with 1,1,2,2-tetrachloroethane- d_2 as the solvent. The red (left) rectangular denotes the signals from $-\text{CH}_2\text{OR}$ and the blue (right) rectangular is from $-\text{CH}_2\text{R}$ attached to BDD units.

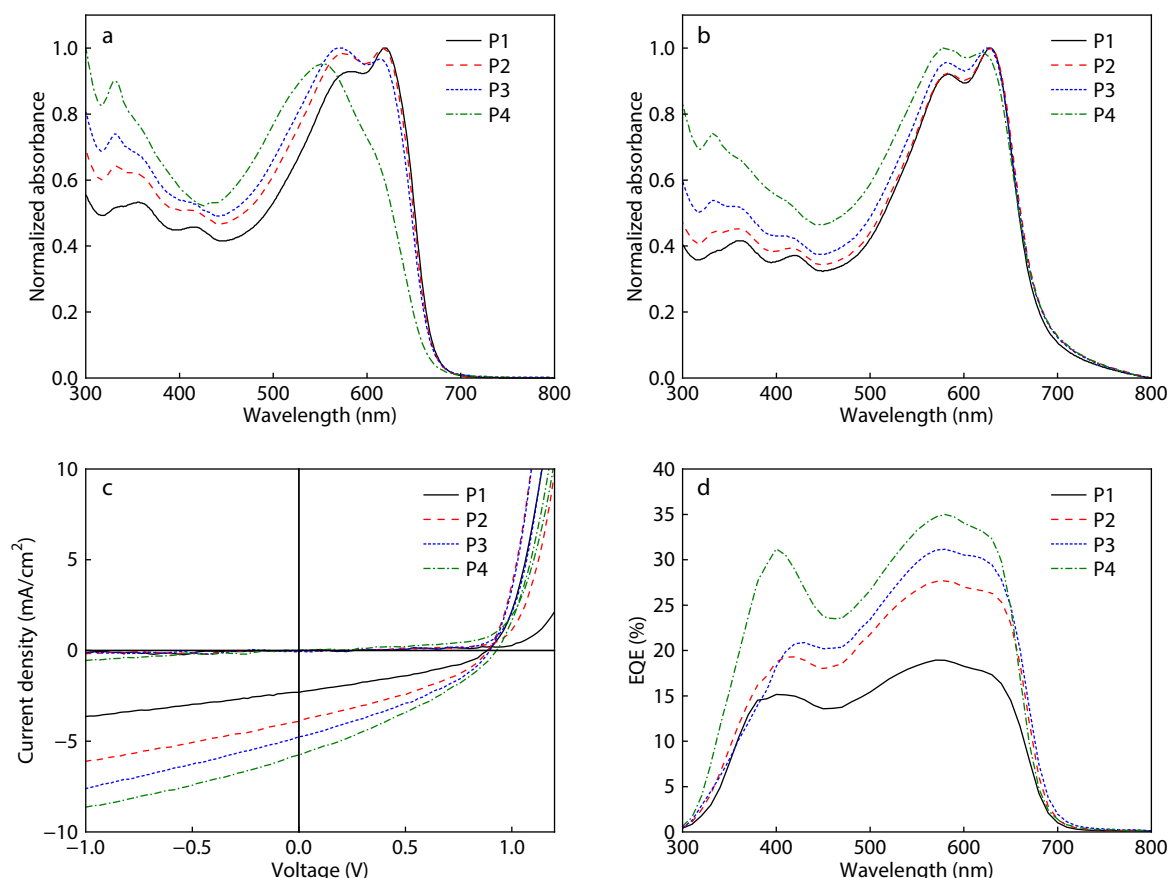


Fig. 2 Optical Absorption spectra of the polymers P1–P4 (a) in solution and (b) in the thin film; (c) *J*-*V* characteristics under simulated AM1.5G condition of optimized SCOSCs based on P1–P4 as the photoactive layers; (d) EQE spectra of the corresponding devices.

may be explained by the less aggregation of conjugated backbones.^[29,35] This would be induced by the steric hindrance of fullerene side units to conjugated backbones in **P4**. However, this behavior is disappeared in thin films. All polymer thin films show red-shift absorption with optical band gaps (E_{g}) of ~ 1.85 eV (Table S1 in ESI). The electrochemical properties of the polymers were studied by cyclic voltammograms (CV) measurement (Fig. S3 in ESI), and the data was summarized in Table S1 (in ESI). They show similar lowest unoccupied molecular orbital (LUMO) levels ($-3.75 \sim -3.81$ eV), while their highest occupied molecular orbital (HOMO) levels are varied from -5.52 eV to -5.72 eV, which may be due to the content changes of the monomer **M1** in the polymers.

These polymers as single photoactive layer were then applied into SCOSCs with an inverted configuration of ITO/ZnO/photoactive layer/MoO₃/Ag. The photoactive layers were spin-cast from CB solution, in which high boiling point

diiodooctane as additive showed a negative effect on photovoltaic performance, while thermal annealing at 150°C could enhance the performance (Table S2 in ESI). Therefore, **P1–P4** based SCOSCs used this optimized condition, in which *J*-*V* characteristics are shown in Fig. 2(c) and the photovoltaic parameters are summarized in Table 1.

It was observed that when increasing the fullerene content, the PCEs were enhanced from 0.71% to 1.71% (**P1** to **P4**), which was mainly due to the enhanced short-circuit current density (J_{sc}) (Table 1). This was also reflected in their external quantum efficiencies (EQEs) as shown in Fig. 2(d), with the photoresponse from 300 nm to 700 nm. **P1** exhibits the maximum EQE of $\sim 15\%$, while EQEs based on **P4** are enhanced to 35%. It is also noted that the EQE contributions both from fullerene side units (300–400 nm) and conjugated backbones (500–700 nm) were enhanced in **P4**-based solar cells, indicating that both of them can equally create charges. For all the

Table 1 Characteristics of optimized SCOSCs based on **P1–P4**.

Photoactive layer ^a	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE ^b (%)
P1	2.31 (2.14 $\pm$ 0.100)	0.883 (0.890 $\pm$ 0.005)	34.75 (35.29 $\pm$ 0.497)	0.71 (0.67 $\pm$ 0.027)
P2	3.90 (3.73 $\pm$ 0.159)	0.887 (0.887 $\pm$ 0.004)	35.09 (34.99 $\pm$ 0.448)	1.21 (1.16 $\pm$ 0.048)
P3	4.75 (4.67 $\pm$ 0.070)	0.895 (0.896 $\pm$ 0.007)	35.35 (34.94 $\pm$ 0.690)	1.50 (1.46 $\pm$ 0.028)
P4	5.75 (5.37 $\pm$ 0.225)	0.927 (0.922 $\pm$ 0.008)	32.22 (32.46 $\pm$ 0.371)	1.71 (1.60 $\pm$ 0.069)

^a The photoactive layers were fabricated from CB solution and thermally annealed at 150°C for 10 min; ^b The highest performance cells. The values in parentheses represent statistics results from 6 independent cells.

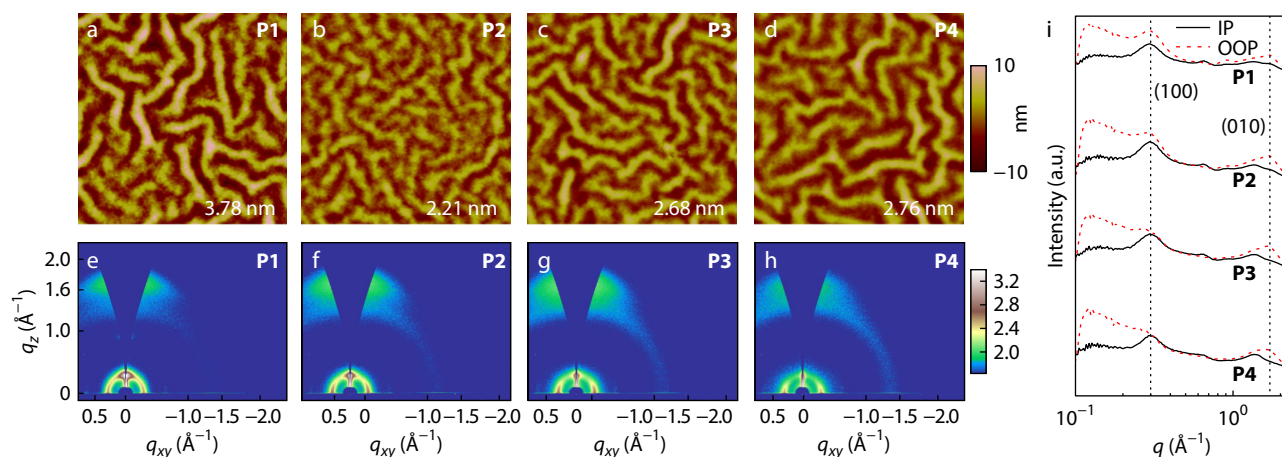


Fig. 3 (a–d) AFM height (3 μm × 3 μm) images and (e–h) GIWAXS patterns of the optimized **P1–P4** thin films. Root mean square (RMS) roughness is also included. (i) The IP and OOP cuts of the corresponding GIWAXS patterns. The (100) and (010) peaks are denoted.

cells, the open-circuit voltages (V_{oc} s) were around 0.883–0.927 V, and the fill factors (FFs) were rather low. We also note that the V_{oc} s increase with fullerene contents increasing, which would be possibly due to the higher acceptor content that facilitates the construction of electron conduction paths and reduces voltage loss.^[47]

In order to study the origination of low PCEs in these cells, we fabricated bulk-heterojunction (BHJ) OSCs by using PBDB-T:PCBM (Fig. S4 in ESI) blends as photoactive layers, in which the ratios of PBDB-T:PCBM were estimated to be consistent with the fullerene contents in the double-cable polymers (Table S3 in ESI). All BHJOSCs provided higher PCEs (1.87%–3.76%) than those of SCOSCs, which is mainly due to the enhanced J_{sc} s and FFs. Interestingly, V_{oc} s in BHJOSCs are slightly low compared to those in SCOSCs. This is different from previous double-cable conjugated polymers based on rylene diimides side units, where they always showed much higher PCEs than the corresponding BHJOSCs.^[32,48] The lower PCEs in fullerene based SCOSCs may be due to the random polymerization strategy and the poor microstructure in thin films, which will be studied in the following section.

We performed space charge limited current (SCLC) measurement to obtain the charge carrier mobilities in these SCOSCs (Fig. S5 and Table S4 in ESI). The hole mobilities in these SCOSCs were in the order of 10^{-4} cm²·V⁻¹·s⁻¹, which is similar to the double-cable polymers with rylene diimide acceptors. However, the electron mobilities were failed to be obtained in our measurement, which might indicate that fullerene units in these polymers cannot form good interpenetrated networks for electron transport.^[29]

We then used atomic force microscope (AFM) and grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements to study the microstructure of **P1–P4** thin films, as shown in Fig. 3. All thin films exhibited large fibril structure with diameters ~100 nm, indicating the large phase separation in these polymers. From GIWAXS, all the polymers exhibited (100) diffraction peaks with $q=0.297$ Å⁻¹ and the diffraction peaks (010) at the out-of-plane (OOP) direction with $q=1.67$ Å⁻¹ (Figs. 3e–3h and Table S5 in ESI). **P1** shows the (100) peaks at both the in-plane (IP) and OOP directions, indicating its mix orientation (both edge-on and face-on) to the

substrate. The intensity of (100) peaks at the OOP direction are gradually reduced and meanwhile the (100) peaks at the IP direction are maintained for **P2–P4**, indicating that the increasing content of fullerene side units enable the polymers to have face-on orientation to the substrate. This is similar to the perylene bisimides based double-cable conjugated polymers.^[35] The coherence lengths (CLs) of (100) peaks at the IP direction seem to be slightly increased, and CLs for (010) peaks are slightly reduced, which should be due to the crystalline change of conjugated backbones. For fullerene side units, we could observe the halo ring at $q\sim 1.4$ Å⁻¹, in which the size of the ring was enlarged when enhancing the content of fullerene. From these results, we infer that the enhanced fullerene contents can make the polymer to show preferentially face-on orientation and meanwhile construct channels for electron transport, explaining the improved PCEs in **P4** based SCOSCs.

CONCLUSIONS

In conclusion, we developed a series of fullerene-contained double-cable conjugated polymers via FP method, in which “donor-acceptor” conjugated backbones were successfully incorporated into the polymers. These polymers exhibited broad absorption spectra from 300–700 nm and aligned energy levels. They were applied into SCOSCs, providing PCEs of 0.71%–1.71%. The low PCEs in these cells revealed the difficulty to realize high-performance in fullerene based double-cable conjugated polymers, which may be due to the relatively low content of fullerene side units and the difficulty to tune the microstructure in these polymers. However, the polymers exhibited poor solubility when enhancing the content of fullerene side units. Therefore, it is important to balance the solubility and fullerene content in these double-cable conjugated polymers in order to further improve the PCEs.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2732-2>.

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