Regioregularity and Electron Deficiency Control of Unsymmetric Diketoppyrrolopyrrole Copolymers for Organic Photovoltaics

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ABSTRACT: Manipulating the electron deficiency and controlling the regioregularity of π-conjugated polymers are important for the fine-tuning of their electronic and electrochemical properties to make them suitable for an organic solar cell. Here, we report such a molecular design of unsymmetric diketoppyrrolopyrrole (DPP) based copolymers with different aromatic side units of either thiophene (Th), pyridine (Py), or fluorobenzene (FBz). The unsymmetric electron acceptors of Th–DPP–Py and Th–DPP–FBz were polymerized with the electron donor of two-dimensional benzothiadiazole (BDT-Th), affording two regiorandom DPP copolymers via sandwiching the centrosymmetric BDT-Th unit by two Th–DPP–Py units in an axisymmetric manner. The extensive characterization through morphology observation, X-ray diffraction, and space-charge-limited current mobilities highlight the case-dependent positive/negative effects of regioregularity and electron deficiency control.

INTRODUCTION

A polymer-fullerene solar cell is a representative framework for organic photovoltaics (OPV),†−§ which has recently evolved into molecular OPV,6−9 nonfullerene OPV,10−14 and ternary-blend OPV.15−19 In general, the development of novel π-conjugated polymers is a matter of great importance for improving the power conversion efficiency (PCE) in OPVs. The first- and second-milestone polymers are highly crystalline regiorregular poly(3-hexylthiophene) (P3HT)20−22 and narrow band gap polymers (NBPs) implemented through the intramolecular charge-transfer transition of covalently bonded electron donor and acceptor units, respectively.23−26 Owing to the great deal of freedom in the molecular design, the NBP strategy has yielded various conjugated polymers for OPV, of which electron-deficient units include isoindigo,27−30 thienopyrroloindene,31−33 benzothiadiazole,34−37 and quinoxaline.38−41

Diketoppyrrolopyrrole (DPP)42−44 is a conventional red dye and has been used as the electron acceptor of NBPs. Generally, the DPP unit has two symmetric thiophene (Th) or furan side units, which results in a flat π-plane and high film crystallinity, leading to PCEs in the range of 6−8% for polymer−fullerene OPVs.45−48 Meanwhile, unsymmetric DPP with Th and thiophenophene (TP)49 or pyridine (Py)50 has exhibited comparable PCEs of 6−8%. Other unsymmetric electron acceptors are fluorinated thiophenophene of PTB751−53 benzothienoisindigo,54−56 and pyridylthiadiazole (PT)57−59

The electron donor of benzothiadiazole (BDT) with asymmetric side units is another example, which is unsymmetric in the direction perpendicular to the polymer backbone.60,61 The unsymmetric structure and regiorandom configuration of copolymer would lead to a good balance between solubility and crystallinity and, in some cases, a highly preferential face-on orientation of the polymer backbone, suitable for OPV devices.62−64 We have previously reported the unsymmetric DPP-based copolymers bearing phenyl (Ph) and Th or TT, exhibiting PCEs of 2.3−2.4%, which were higher than the symmetric analogue of Ph-DPP-Ph (0.45%).62 Such an unsymmetric DPP bears a half-distorted π-plane due to the steric hindrance between the proton of Ph and oxygen of DPP, which provides very good solubility (~100 mg mL−1 in toluene). However, the polymer crystallinity was drastically decreased in both pristine films and bulk heterojunction (BHJ) films blended with [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). Accordingly, the increase in the π-plane coplanarity, tuning of electron deficiency (and intramolecular electro-negative interaction), and/or the control of regioregularity are expected to be the next rational modifications of unsymmetric DPP to improve the crystallinity and PCE.

In this study, we report the synthesis and characterization of the unsymmetric Th−DPP−Ar, where Ar is either Py or fluorobenzene (FBz). The Th−DPP−Py unit displayed a more planar structure than the previous counterpart Th−DPP−Ph because the C−H unit, which causes a significant steric...
hindrance, was replaced by a less steric nitrogen atom. On the other hand, the C–F unit of Th–DPP–FBz was introduced to produce deepening of the highest occupied molecular orbital (HOMO) and increasing of the open-circuit voltage (V_{OC}); meanwhile, the fluorine atom, larger than hydrogen, might lead to a more twisted structure. Because the improved PCE of 3.75% was achieved for the regiorandom NBP, composed of Th–DPP–Py as the electron acceptor and two-dimensional benzobisthiophene appending alkyliophene side units (BDT-Th)\textsuperscript{53,64} as the electron donor, we synthesized a regioregular DPP copolymer via sandwiching the centrosymmetric BDT-Th unit by two Th–DPP–Py units in an axisymmetric manner. Although a moderate space-charge-limited current (SCLC) hole mobility of 4.1 × 10\textsuperscript{-4} cm\textsuperscript{2} (V s\textsuperscript{-1}) was found in the pristine film of regioregular DPP, the PCE of BHJ-OPV decreased to 2.56%. We performed a comparative study on the reason, fl

\textbf{RESULTS AND DISCUSSION}

Unsymmetric and regiorandom copolymers of PPy and PFBz were synthesized via Stille cross-coupling of a bis-stannylated BDT-Th with the bis-brominated Th–DPP–Py and Th–DPP–FBz, respectively, as shown in Figure 1. The chemical structure of PBz is also provided, which has unsymmetric Ph and Th side units and serves as the reference for PPy and PFBz. Among these regiorandom copolymers, PPy exhibited the highest PCE (vide infra). Therefore, we examined the regioregularity control for the Th–DPP–Py unit. In fact, two types of molecular designs are possible for regioregular polymers, as shown in Figure 2a, where the unsymmetric unit is positioned in the same direction (type I), while a pair of unsymmetric units is repeated in alternating fashion (type II).\textsuperscript{65} Regioregular P3HT, which has a head-to-tail regioregularity (typically >90\%), is categorized into type I, which is synthesized by, e.g., Grignard metathesis method (GRIM), based on the reactivity difference in the hydrogen atoms at the 2 and 5 positions of 3-alkliyliophene.\textsuperscript{55,66} Another type I polymer composed of cyclopentadiithiophene and PT reported by Bazan et al. also exploits the difference in the reactivity of bromine atoms of an unsymmetric PT unit.\textsuperscript{57} For the same reason, fluorinated thienothiophene\textsuperscript{53} is applicable to type I regioregular polymers, in which the preparation of monostannylated and monobrominated monomer is essential for the subsequent Stille cross-coupling. However, such an unsymmetrically labeled monomer is difficult for our polymer to synthesize because of the large size of the acceptor that weakens the difference in proton (or bromine) reactivity. Therefore, one bromine atom was introduced at the pyridine unit of the unsymmetric DPP by using a monobrominated compound (5-bromo-2-cyanopyridine) as the starting chemical, which enables the synthesis of a type II regioregular polymer (Supporting Information). The chemical structure of the resultant polymer RR-PPy and its synthetic scheme are shown in Figure 2b. It should be noted that our DPP unit that encompasses unsymmetry and regioregularity is large in size, which is in contrast to the other type II polymers based on small-sized PT\textsuperscript{57,58} and thienothiophene.\textsuperscript{67−71}

Figure 3a shows the photoabsorption spectra of PPy, PFBz, and RR-PPy in diluted chlorobenzene solutions and films. Although all the polymers exhibited mostly unchanged absorption maxima, the shoulder peaks in the longer-wavelength region were observed in PPy and RR-PPy. This is suggestive of their more extensive conjugation and higher crystallinities, as compared with PFBz. Figure 3b displays the electrochemical properties of the polymers, including HOMO levels, as evaluated using photoelectron yield spectroscopy (PYS) and the band gap energy (E\textsubscript{g}) estimated from the onset of the photoabsorption spectra in the films (Figure S1). The lowest unoccupied molecular orbital (LUMO) levels were calculated by adding E\textsubscript{g} to the HOMO levels. PFBz exhibited the widest E\textsubscript{g} of 1.80 eV along with the deepest HOMO level (−5.52 eV) and the shallowest LUMO level (−3.72 eV) because of the electron-withdrawing nature of the fluorine atom. The increased E\textsubscript{g} of PFBz compared with the nonfluorinated analogue (PBz, E\textsubscript{g} = 1.67 eV) was further rationalized by the more twisted backbone structure of PFBz, as calculated by density functional theory (DFT), shown in Figure 3c. The dihedral angle between the DPP and
fluorinated Ph is 39°, which is larger than that of PBz (25°).62 On the other hand, PPy and RR-PPy showed mostly identical electrochemical properties, i.e., HOMO at −5.43 and −5.47 eV and $E_g$ of 1.62 and 1.63 eV, respectively, indicating that the regioregularity did not significantly impact the energetics of intramolecular charge transfer interaction, similar to the one reported for regioregular type II polymers.57−71 These $E_g$ values are 0.4−0.5 eV narrower than that of the reference PBz.62 In addition to the increased electron-accepting ability of pyridine, a narrow $E_g$ is supported by a more coplanar backbone (dihedral angle ∼2°, Figure 3c) and the appearance of a distinct shoulder peak (Figure 3a). The weight-averaged molecular weights ($M_w$) and polydispersity indices (PDI) of the polymers were characterized by size exclusion chromatography (Figure S2) and showed moderate values ($M_w = 10$ kg mol$^{-1}$ for PFBz, 80 kg mol$^{-1}$ for PPy, and 83 kg mol$^{-1}$ for RR-PPy). These electrochemical and polymeric properties are listed in Table 1. The inverted-type OPV devices (indium tin oxide (ITO)/ZnO/active layer/MoO$_3$/Ag) were fabricated from the chlorobenzene solutions with 3 vol % 1,8-diiodooctane as the solvent additive. We surveyed the processing conditions including thermal annealing (120 °C for 10 min) and the blend ratios (copolymer/PCBM = 1:1, 1:1.5, 1:2, and 1:3) (Tables S1). The optimized PFBz:PCBM device showed a PCE of 0.18% (average: 0.15%), which considerably suffered from the small short-circuit current density ($J_{sc} = 0.85$ mA cm$^{-2}$) and fill factor (FF = 0.29) (Figure 4a and Table 2). In stark contrast, PPy:PCBM exhibited a PCE of 3.75% (average: 3.61%), which is a great improvement compared with the reference (2.30% for the PBz:PCBM).62 The increased $J_{sc}$, owing to the wide photoabsorption up to ∼800 nm, and the upward shift in external quantum efficiency (EQE; Figure 4b) are responsible for the improved PCE, although the FF is still not high (0.45). Regretfully, RR-PPy:PCBM resulted in a lower PCE of 2.56% (average: 2.28%) than PPy, mainly caused by the decrease in $J_{sc}$ and EQE. The VOC values (0.72, 0.78, and 0.81 V for PFBz, RR-PPy, and PPy, respectively) are in a reverse order of their HOMO levels (−5.52, −5.47, and −5.43 eV for PFBz, RR-PPy, and PPy, respectively). This discrepancy is due to the low FF (less than 0.45) associated with the large series resistance, as seen from the slight slopes of the $J$−$V$ curves in Figure 4a.

In previous reports, all of the regioregular type II polymers showed an improved PCE compared with the regiorandom analogues.57−71 Despite the limited number of cases, we speculate that the positive effect of regioregularity control (improvement in crystallinity) is deteriorated for the long-shaped repeating unit, as in our RR-PPy. This is because the acceptor unit of previous regioregular polymers is one unsymmetric aromatic ring in the conjugation direction. The PCE values among the four polymers (in the order of low PFBz, PBz, RR-PPy, and high PPy) indicated a good agreement with the transient photoconductivity intensities of blend films measured by Xe-flash TRMC (Figure S3),72 suggesting that the crystallinity and free charge-carrier generation3−7 in RR-PPy are lower than those in regiorandom PPy.

Surface morphologies of pristine and blend films were observed by atomic force microscopy (AFM) as shown in Figure 5. While PPy and RR-PPy displayed moderate BHJ
The π more crystalline and face-on features, as compared with PFBz. pristine film (Figure 5b). Such an anomaly was not observed in pristine polymer films (Figure 5a). Fluorination of NBP is a rational design for the fine-tuning of HOMO/LUMO levels and facilitating the electron transfer to n-type semiconductor at the p/n interface owing to the more localized LUMO as opposed to nonfluorinated analogue. Conversely, the large electro-negativity and hydrophobic nature of fluorinated analogue. Conversely, the large electro-negativity and hydrophobic nature of fluorine atom may lead to a coarse BHJ morphology, increased amorphous nature, and/or change in polymer orientation. Although a reason for the pin-hole formation in the PFBz:PCBM film is unclear, fluorination of our DPP polymers caused a negative electronic character, which is related to the PCE values. The mobility balance (vide infra) may be another reason for the low quality of the BHJ morphology without large aggregations, PFBz showed unusual pin-holes (black spots in the height image), which is in contrast to the smooth surface of nonfluorinated PBz:PCBM film (Figure 5b). The left, center, and right panels correspond to PPy, PFBz, and RR-PPy, respectively.

The two-dimensional grazing-incidence X-ray diffraction (2D-GIXRD) image of PFBz pristine film revealed its amorphous nature without π−π stacking diffraction and orientation (Figures 6a,b). In contrast, PPy and RR-PPy pristine films exhibited a weak but clear π−π stacking diffraction in the out-of-plane direction, indicative of their more crystalline and face-on features, as compared with PFBz. The π−π stacking distance (dπ) and coherence length (Lc) calculated using the Scherrer’s relation were 0.384 and 1.2 nm for PPy and 0.391 and 1.0 nm for RR-PPy, respectively (Table 1). These dπ values are larger than those of the crystalline polymers (ca. 0.35–0.37 nm); thus, even PPy and RR-PPy are categorized into low-crystalline and nonoriented polymers. The interlamellar distance (dIL) and its coherence length (LIL) did not vary significantly among the polymers (dIL = 1.62–1.73 nm and LIL = 3.5–3.9 nm), which was also confirmed by the one-dimensional XRD measurements (dIL = 1.59–1.62 nm and LIL = 3.1–3.4 nm in Figure S4). Notably, the copolymer:PCBM blend films turned to almost completely amorphous features without any orientation, as shown in Figure 6c,d. This result is consistent with the insufficient PCE values of OPV devices (0.18–3.75%) and SCLC mobilities (vide infra).

SCLC hole (μh) and electron (μe) mobilities were evaluated for the device-optimized BHJ films (J−V curves are shown in Figure S5). As listed in Table 2, the values of μh (2.3–9.1) × 10−6 cm2(V s)−1 and μe (0.98–8.5) × 10−4 cm2(V s)−1 are roughly correlated with the PCE values. The mobility balance (μh/μe−1) was not a good explainable parameter; however, the low μe was less than 0.03 could be one of the reasons for the low FF (<0.45) observed in all the devices. The correlation of μh vs PCE was degraded when the reference PBz was included (Figure S6). On the contrary, a good correlation between μe and PCE was found even in the presence of Pb, suggesting that the predominant factor of PCE is μe similar to the case of our previous regiondominant DPP polymers. Both μh and μe were categorized into low-crystalline and nonoriented polymers. The interlamellar distance (dIL) and its coherence length (LIL) did not vary significantly among the polymers (dIL = 1.62–1.73 nm and LIL = 3.5–3.9 nm), which was also confirmed by the one-dimensional XRD measurements (dIL = 1.59–1.62 nm and LIL = 3.1–3.4 nm in Figure S4). Notably, the copolymer:PCBM blend films turned to almost completely amorphous features without any orientation, as shown in Figure 6c,d. This result is consistent with the insufficient PCE values of OPV devices (0.18–3.75%) and SCLC mobilities (vide infra).

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| polymer (p:n) | L/nm | JSC (JSC) /mA cm−2 | VOC/V | FF | PCE/% | PCEmax (%) | μh/cm2(V s)−1 | μe/cm2(V s)−1 |
|---------------|------|--------------------|------|----|-------|------------|--------------|--------------|
| PBz (1:1)     | 70   | 6.50 (6.35)        | 0.88 | 0.44| 2.30  | 1.83       | 2.1 × 10−6   | 1.9 × 10−6   |
| PPy (1:2)     | 120  | 10.2 (8.72)        | 0.81 | 0.45| 3.75  | 3.61       | 9.1 × 10−6   | 8.5 × 10−4   |
| PFBz (1:1.5)  | 70   | 0.85 (0.85)        | 0.72 | 0.29| 0.18  | 0.15       | 2.3 × 10−4   | 9.8 × 10−5   |
| RR-PPy (1:2)  | 100  | 7.14 (6.29)        | 0.78 | 0.45| 2.56  | 2.28       | 6.4 × 10−6   | 2.1 × 10−4   |

“Inverted cell (ITO/ZnO/active layer/MoO3/Ag) under 1 sun (100 mW cm−2). Taken from the literature (named as P2 in the reference).

Table 2. Summary of Polymer:PCBM OPV Performances and SCLC Mobilities

Figure 5. AFM height images of (a) pristine copolymer films and (b) copolymer/PCBM blend films. The left, center, and right panels correspond to PPy, PFBz, and RR-PPy, respectively.

Figure 6. (a) 2D-GIXRD images and (b) their diffraction profiles of the pristine copolymer films. (c) 2D-GIXRD images and (d) their diffraction profiles of the copolymer:PCBM blend films. Out-of-plane (OOP, red line) and in-plane (IP, blue line) profiles are shown in (b) and (d), respectively. The left, center, and right panels correspond to PPy, PFBz, and RR-PPy, respectively.

DOI: 10.1021/acsomega.9b02146
ACS Omega 2019, 4, 15645–15652
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and \( \mu_e \) in the blend films were decreased for RR-PPy compared with PPy; however, it should be noted that \( \mu_e \) of pristine RR-PPy film \((2.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\) is approximately 2-fold of PPy \((9.3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\) and 70-fold of PFBz \((3.0 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\) (Table 1 and Figure S7). At least in the pristine film, regioregularity control is beneficial to the improvement in hole mobility. Thus, the unsatisfactory result in RR-PPy OPV is due to the decrease in \( \mu_e \) when PCBM is blended in, which is concomitant with the low \( \mu_e \) caused by the low crystallinity of the counter phase of the p-type RR-PPy.

## CONCLUSIONS

We synthesized and characterized unsymmetric, regiorandom DPP polymers (PPy and PFBz), whose electron deficiencies were modulated by introducing nitrogen or fluorine into the Ph part of the reference (PBBz). The PCE of PPy was improved to 3.75\% compared to that of PBBz (2.30\%), while that of PFBz was as low as 0.18\% because of its considerably low crystallinity and low \( \mu_e \) and \( \mu_h \). The type II regioregular DDP polymer of RR-PPy exhibited a decreased PCE of 2.56\%, whereby the PCEs of these polymer:PCBM OPVs were likely governed by \( \mu_e \). Although \( \mu_e \) was the highest for pristine RR-PPy, it was drastically decreased in the PCBM-blend film because of the degradation in crystallinity and orientation. With regards to polymer design, this study suggests that the regioregularity control does not necessarily lead to improved OPV performance, which is possibly attributable to cases of large-sized unsymmetric acceptors.

## EXPERIMENTAL SECTION

**General Measurement.** Steady-state photoabsorption spectra were recorded using a Jasco V-570 UV–vis spectrophotometer. The molecular weight (weight-averaged: \( M_w \)) and polydispersity index (PDI) of polymers were measured using the size exclusion chromatography (gel permeation chromatography:GPC, a Shimadzu Corp. LC-20AT/CBM-20A/CTO-20A/SPD-M20A) with polystyrene standards in hot chloroform \((40{^\circ}\text{C})\) as an eluent. Photoelectron yield spectroscopy (PYS) of the polymer films on indium–tin–oxide (ITO) glass was performed using Bunko Keiki BIP-KV2016K. 2D-GIXD experiments were performed on the beam line BL46XU at the SPring-8 \((12.39 \text{ keV}, \lambda = 1\ \text{Å} \text{X-ray})\). The 2D-GIXD patterns were monitored with a 2D image detector (Pilatus 300 K). Atomic force microscopy (AFM) was performed using a Bruker Innova AFM microscope. Differential scanning calorimetry (DSC) was carried out using a Netzsch DSC204F1 Phoenix differential scanning calorimeter under \( N_2 \) at 10 \({^\circ}\text{C} \text{ min}^{-1} \) (sample weight \( \sim 2 \text{ mg} \)). Thicknesses of the polymer and blend films were measured using a Bruker Dektak XT surface profiler. Xe-flash time-resolved microwave conductivity (TRMC) was performed for the polymer:PCBM films prepared on a quartz substrate. The microwave frequency and excitation light were \( \sim 9 \text{ GHz} \) and a white light from a Xe-lamp (pulse width \( \sim 10 \mu\text{s} \)). Details are in the reference.76

**Synthesis of Polymers.** Symmetric and unsymmetric DPP monomers were synthesized according to the references.79,90,50,62 The synthetic details including the NMR, elementary analysis, and matrix-assisted laser desorption ionization time-of-flight massspectrometry are provided in the Supporting Information. The polymers (PPy, PFBz, and RR-PPy) were synthesized by Stille coupling with the \( (\text{PPh}_3)_2\)Pd catalyst from the Br-DPP-Br monomer and (Me,Sn)-(BDT-Th)-(SnMe3) monomer. The yields were 62\% for PPy, 47\% for PFB, and 62\% for RR-PPy.

**OPV.** After cleaning an ITO/glass substrate, a ZnO layer was fabricated by spin-coating with a ZnO precursor solution \((0.1 \text{ g mL}^{-1} \text{ zinc acetate dihydrate and 0.028 g mL}^{-1} \text{ ethanolamine in 2-methoxyethanol})\) followed by annealing on a hot plate at 200 \({^\circ}\text{C} \text{ for 30 min} \). On top of the ZnO layer, a BHJ layer was spin-cast in a nitrogen glovebox. Subsequently, an anode \((10 \text{ nm MoO}_3 \text{ and 100 nm Ag})\) was deposited through a shadow mask by thermal evaporation in a vacuum chamber. The device configuration was an ITO \((120–160 \text{ nm})/\text{ZnO (30 nm)}/\text{BHJ/MoO}_3/\text{Ag (100 nm)}\) with an active area of 7.1 \text{ mm}^2. The solar cell characteristics were measured using an ADCMT Corp., 6241A source meter unit under air mass 1.5 G solar illumination at 100 mW cm\(^{-2}\) (1 sun, monitored by a calibrated standard cell, Bunko Keiki SM-250KD) from a 300 W solar simulator (SAN-EL Corp., XES-301S). The EQE spectra were recorded using a Bunko Keiki model BS-520BK equipped with a Keithley model 2401 source meter. The monochromatic light power for EQE measurements was calibrated by a silicon photovoltaic cell of a Bunko Keiki model S1337-1010BQ.

**SCLC.** The SCLC devices were fabricated in the same manner as the OPV devices. Hole-only device was ITO/PEDOT:PSS/active layer \((100–200 \text{ nm})/\text{Au}\) and electron only device was Al/active layer \((\sim 200 \text{ nm})/\text{LiF/Al}\). The mobility was determined by fitting a current density–voltage curve by the Mott–Gurney law, \( J = 9e_\text{D}d_\text{f}\mu V^2(8L^3)^{-1} \), where \( e_\text{D}, d_\text{f}, \mu, V, \) and \( L \) are the permittivity of the material, the mobility, the voltage drop across the device, and the thickness of the active layer, respectively.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02146.

Experimental details on polymer synthesis; UV–vis photoabsorption and PYS spectra (Figure S1); GPC profiles (Figure S2); transient photocconductivity of Xe-flash TRMC (Figure S3); AFM height images of pristine polymer films (Figure S4); XRD profiles of pristine polymer films (Figure S5); 2D-GIXD images of the pristine films (Figure S6); SCLC curves of polymer:PCBM blend films (Figure S7); Plots of PCEs vs \( \mu_e, \mu_h \), and \( \mu_e, \mu_h \) (Figure S8); SCLC curves of polymer films (Figure S9); \(^1\text{H} \) NMR spectrum of PFBz monomer (Figure S10); \(^1\text{H} \) NMR spectrum of PPy monomer (Figure S11); and \(^1\text{H} \) NMR spectrum of the RR-PPy monomer (Figure S12) (PDF)

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### Notes

The authors declare no competing financial interest.
ACKNOWLEDGMENTS

This work was supported by the PRESTO program (Grant no. JPMJPR15N6) from the Japan Science and Technology Agency (JST) and the Japan Society for the Promotion of Science (JSPS) with the KAKENHI Grant-in-Aid for Scientific Research (A) (Grant no. JP16H02285). We thank Prof. Itaru Osaka at Hiroshima University and Dr. Tomoyuki Koganemura at JASRI for the support of 2D-GIXD experiments at SPring8 (2018A1568, 2018B1595, and 2019A1765).

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