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Fine-Tuning Solid-State Ordering and Thermoelectric Performance of Regioregular P3HT Analogues by Sequential Oxygen-Substitution on Carbon Atoms along the Alkyl Side Chains

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Conjugated polymers in thin films tend to orient their backbones in respect to substrates through self-assembly when processed from a solution. Molecular packing orientation and crystallinity of polymer crystals have been found to play a critical role on their electrical performance. Taking advantage of the shorter bond length and the smaller rotation energy of the CH₂-O bond than the CH₂-CH₂ bond in an alkyl chain, a side-chain engineering strategy is reported by sequential oxygensubstitution on carbon atoms from the y position outwards along the hexyls in regioregular poly(3-hexylthiophene) (RR-P3HT). The subtle disparity between CH₂-O and CH₂-CH₂ bond is found to be able to fine-tune the solid-state organization of corresponding RR-P3HT analogues, namely poly(3-(2-propoxyethyl)thiophene) (P3POET), poly(3-(3the ethoxypropyl)thiophene) (P3EOPT) and poly(3-(4-methoxybutyl)thiophene) (P3MOBT). The evolution of film microstructures is observed when doping with FeCl₃ in nitromethane at room temperature, so are their thermoelectric performance. The highest power factor is 19 µW m⁻¹ K⁻² observed for doped P3POET film, which presents the dominant edgeon orientation with the strongest crystallinity and the closest π - π stacking. At the doping time corresponding to the optimized power factors (PF) for each polymer, the doped P3POET film maintains both relatively high Seebeck coefficient (S) and electrical conductivity (σ) close to their maximum values, while the other polymers give either higher S and much lower σ (P3HT) or higher σ but much lower S (P3EOPT and P3MOBT). The square dependence of PF on S together with higher σ amplifies the power factor value for P3POET, which is almost 2 times compared to the other polymers (11-13 μ W m⁻¹ K⁻²).

1. Introduction

Owing to their tunable optoelectronic properties, thermal stability and mechanical flexibility, conjugated polymers have been actively employed in the field of organic electronics by various cost-effective solution-processing technologies.¹⁻⁶ Such tunability has been incessantly witnessed by manipulating their chemical structures and physicochemical properties in conjunction with device parameters towards expected performance output. Deep understanding of the fundamental structure-property-performance correlations has therefore been significantly advanced over the past years.^{4, 7-11} The knowhow could also be readily applied in materials design and fabrication of lightweight, flexible and low-cost organic thermoelectrics (OTE). Thus, introducing conjugated polymers

among parameters of S, σ , and κ by manipulating phonons and

electrons at nanoscale to enhance the ZT value.^{13, 19} On the

other hand, although the thermal conductivity of organic

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^{c.} Department of Physics, University of Michigan, Ann Arbor, MI 48109, USA. Electronic Supplementary Information (ESI) available: [detailed information on materials, measurement and instrumentation, ¹H-NMR spectra, TGA, CV curves, powder XRD patterns, neutral film GIWAXS profiles and doping time dependent Raman spectra of the polymers and the collection of the optimized thermoelectric performance of the polymers at r.t. doped with different concentrations of FeCl₃/CH₃NO₂ solution]. See DOI: 10.1039/x0xx00000x

C Accepted Manuscr mistrv into thermoelectric applications at moderate temperatures has attracted an increasing attention in recent years.¹²⁻¹⁷ The thermal-to-electrical energy conversion efficiency for a given semiconducting material is generally evaluated by its dimensionless figure of merit defined as $ZT = S^2 \sigma T / \kappa$, where S (V **Waterials** K⁻¹) is the Seebeck coefficient, σ (S m⁻¹) is the electrical conductivity, T is the absolute temperature in Kelvin, and κ (W m⁻¹ K⁻¹) is the thermal conductivity.¹⁸ The Seebeck coefficient is directly related to the density of states. The electrical conductivity is expressed as $\sigma = nq\mu$, where n (cm⁻³) is the carrier density, q is the carrier charge, and μ (cm² V⁻¹ s⁻¹) is the carrier mobility. The combined contribution from the lattice (κ_L) and electron (κ_E) to heat transport constitutes the overall thermal conductivity. The product of $S^2\sigma$ is defined as the power factor (PF), usually specified in μW m⁻¹ K⁻² and indicative of the electrical power that can be generated by a thermoelectric material. What is the most exasperating is the strong adverse interdependence among S, σ , and κ , which imposes restrictions on how large ZT can be achieved. In particular, as n increases, the increasing σ and κ are accompanied by a decreasing S.¹⁸ Optimizing ZT thus stands as a grand challenge. Considerable efforts have been exerted on the structure design and/or processing of materials so as to decouple the interdependence

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semiconductors is much lower $(0.1 - 1 \text{ W m}^{-1} \text{ K}^{-1})$ compared to their inorganic counterparts,²⁰⁻²⁴ it is quite challengeable to be measured, especially in the in-plane direction. Moreover, the thermal conductivity of organic semiconductors, including polymers, is mostly closer to that of a phonon glass.¹⁸ Consequently, it is the *PF* that is usually determined instead of the *ZT* to assess the thermoelectric competency of semiconducting polymers.

Conjugated polymer paradigms within various organic electronic applications have been reiterating the critical role of molecular ordering and orientation as a controlling factor to achieve desired organization for high-performance.²⁵⁻³⁴ Specifically, the edge-on orientated crystalline lamellae could be more favorable for efficient in-plane charge transport as desired in organic field effect transistors, whereas the face-on orientated lamellae could facilitate the out-of-plane charge transport as desired in polymer solar cells. Since the charge transport proceeds predominantly within the lamellae (either along the π - π stacking direction or along the polymer backbones), in some cases, an intermixing orientation textile could even reduce the transport anisotropy, leading to a higher charge transport in specific directions. Grazing incidence wideangle X-ray scattering (GIWAXS) has become a powerful tool for microstructure characterization of polymers in film.³⁵⁻³⁷ The importance of film microstructures has also been demonstrated in recent reports on polymer thermoelectric properties.^{38, 39} For example, besides introducing charge carriers that may form polarons or bipolarons and perhaps even a mixture of the two, the electrical transport properties also depend on the structural organization of semiconducting polymers spanning the regime from the molecular scale to the macroscale in solid state.40 However, given the fact that the optimal solid-state ordering of conjugated polymers within a specific device application can only be reached by trial and error, and is largely materials dependent, the task to directly attain desired solid-state ordering is quite challenging. The introduction of charge carriers within OTE devices is unexceptionally implemented by electrical doping on organic materials so far. There is no secret that choosing the right dopant and doping method (by vapor or solution) is critical to the control of film morphology.²¹ From a molecular engineering point of view, the conjugated backbone and side chains (offering the solubility for processing) of a conjugated polymer have a significant impact on molecular ordering and orientations in thin films. Janáky et al studied the effect of side chain length on the supramolecular structure and the electrical properties.⁴¹ Bazan et al studied the effect of counterions species at side chain and the side chain length on the conductivity and thermopower of self-doped conjugated polyelectrolytes.42 How molecular engineering on conjugated backbone and/or side chain could play the role for OTE polymers in affecting their electronic structure and film microstructure involved in thermoelectric conversion still remains beyond reach. To realize the potential of semiconducting polymers for thermoelectrics, the relationship between the chemical structure, morphology, and the resulting thermoelectric performance needs to be comprehensively understood.

In this contribution, we elucidate the evolution vof molecular packing and thermoelectric properties of p-doped9/regionegular poly(3-hexylthiophene) (RR-P3HT) analogues by engineering the side hexyl chains as indicated in Chart 1. RR-P3HT has evolved as a benchmark polymer for OTE research as well as PEDOT:PSS due to its ready availability and tendency to form ordered lamellar structures in films by interchain stacking.^{41, 43-49} Herein, sequential oxygen substitution on carbon atoms along the side hexyl chains was rationally adopted to fine-tune intermolecular interactions of polymers and to explore their effects on materials physicochemical properties, film microstructures, and OTE performance. Commercial RR-P3HT was also employed as a reference to prompt such investigations. It has been found that the energy barrier of the rotation of O-CH₂ bonds (E = 0.08 eV) is slightly smaller than that of CH_2 - CH_2 bonds (E = 0.11 eV) in an alkyl chain. Meanwhile, the length of CH₂-O σ bond (1.42 Å) is a little bit shorter than that of the CH₂-CH₂ σ bond (1.54 Å).⁵⁰⁻⁵² Such fine disparities could render the singly O-substituted chains more flexible without transforming its aliphatic property relative to the hexyl. A fine evolution of polymer film microstructures could be expected when an oxygen atom substitutes a carbon atom outwards along the side hexyl chains within P3HT. To observe the effect of sequential O-substitution along the side chain on OTE properties, the conventional oxidation doping method by soaking polymer films in FeCl₃ solution in nitromethane for varied time durations was used to make them electrically conducting for OTE measurements at room temperature. Thus, this work has focused more on the effect of side chain engineering on solid-state ordering and OTE performance than on the doping method. Indeed, the evolution of aggregation microstructure is observed accordingly in response to such side chain engineering. When immersion-doped with FeCl₃ in nitromethane at an optimized concentration at room temperature, the film microstructures evolved in comparison to that of their corresponding undoped films. Moreover, the characteristics of charge carriers in the polymer films vary with the increasing doping time, and so do the parameters of S, σ and PF.



2. Experimental Section

2.1 Materials and general information on characterizations

3-Bromothiophene was purchased from Zhejiang Shou & Fu Chemical Co., Ltd.. 2-Propynol was purchased from Beijing Zhongketuozhan Chemical Technology Co., Ltd.. RR-P3HT was purchased from Rieke Specialty Conducting Polymers. 2-Bromo-3-methylthiophene (2), 2-bromo-3-(bromomethyl)thiophene (3), 3-(2-propoxyethyl)thiophene (6), and 4-(3-thienyl)-3butyne-1-ol (13) were prepared according to standard literature

procedures.⁵³⁻⁵⁶ All other chemicals were purchased from J & K and Energy Chemicals and used as received unless noted otherwise. Dry *n*-butanol was obtained by drying with NaOH pellets under reflux before distillation under nitrogen. Anhydrous THF were prepared by standard distillation procedures with sodium and benzophenone prior to use. General information on instrumentation and characterizations can be found in Electronic Supplementary Information.

2.2 Synthesis

2-Bromo-3-(butoxymethyl)thiophene (4). Sodium (2.1 g, 91.0 mmol) was added into a round-bottom flask containing 34 mL of dry n-butanol under nitrogen. The mixture was stirred at room temperature until the sodium was consumed. 2-Bromo-3bromomethylthiophene (7.58 g, 29.6 mmol) was then added dropwise. The solution was stirred at room temperature overnight. The resulting solution was poured into water and extracted with ethyl ether. After drying over anhydrous MgSO₄, the extraction was filtered and concentrated. The crude product was distilled under reduced pressure to obtain 4.94 g of the pure product (yield, 67%). ¹H-NMR (500 MHz, CDCl₃), δ (ppm): 7.23 (d, J = 4.10 Hz, 1H), 6.98 (d, J = 3.15 Hz, 1H), 4.43 (s, 2H), 3.46 (t, J = 6.00 Hz, 2H), 1.58 (m, 2H), 1.39 (m, 2H), 0.91 (t, J = 7.13 Hz, 3H). ¹³C-NMR (125 MHz, CDCl₃), δ (ppm): 138.60, 128.18, 125.82, 110.80, 70.22, 66.76, 31.74, 19.32, 13.86. GC-MS: C₉H₁₃OSBr, [M]⁺ calc.: 247.99, found: 247.93 (M), 174.75 (M-C₄H₉O).

2-Bromo-3-(2-propoxyethyl)thiophene (7). Similar to the preparation of 2-bromo-3-methylthiophene (**2**), the compound was prepared from 3-(2-propoxyethyl)-thiophene (**6**) and purified by distillation under reduced pressure with a yield of 69%. ¹H-NMR (500 MHz, CDCl₃), δ (ppm): 7.19 (d, *J* = 4.90 Hz, 1H), 6.87 (t, *J* = 2.80 Hz, 1H), 3.59 (t, *J* = 6.75 Hz, 2H), 3.40 (t, *J* = 6.40 Hz, 2H), 2.86 (t, *J* = 6.65 Hz, 2H), 1.59 (m, 2H), 0.91 (t, *J* = 7.20 Hz, 3H). ¹³C-NMR (125 MHz, CDCl₃), δ (ppm): 138.47, 128.63, 125.20, 109.80, 72.60, 69.62, 29.99, 22.90, 10.56. GC-MS: C₉H₁₃OSBr, [M]⁺ calc.: 247.99, found: 247.89 (M), 174.80 (M-C₄H₉O).

3-(3-Thienyl)-2-propyn-1-ol (9). To a two-neck round-bottom flask was added in Pd(PPh₃)Cl₂ (1.01 g, 5.0 mmol), PPh₃ (2.62 g, 10.0 mmol), Cul (1.91 g, 10.0 mmol), 3-bromothiophene (16.3 g, 100.0 mmol), and 30 mL of anhydrous dimethyl formamide (DMF) under nitrogen. After stirring for 10 min, 100 mL of anhydrous diisopropylamine and 2-propyn-1-ol (11.2 g, 200.0 mmol) was added in. The mixture was then heated to reflux overnight. After cooling down to room temperature, the mixture was filtered and the filtrate was concentrated. After removal of the residual solvent of DMF by distillation under reduced pressure, the crude product was further purified by silica gel column chromatography eluted by petroleum ether/ethyl acetate (3:1, v/v) to furnish the pure product (yield, 75%). ¹H-NMR (500 MHz, CDCl₃), δ (ppm): 7.45 (d, *J* = 2.00 Hz), 7.26 (dd, J = 3.05 Hz, 2.40 Hz, 1H), 7.11 (d, J = 3.95 Hz, 1H), 4.48 (s, 2H), 2.04 (s, 1H). ¹³C-NMR (125 MHz, CDCl₃), δ (ppm): 129.77, 129.08, 125.34, 121.50, 86.86, 80.82, 51.53. GC-MS: C7H6OS, [M]⁺ calc.: 138.01, found: 138.01 (M).

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3-(3-Ethyoxyl-1-propynyl)thiophene (10). The vipreparation procedure was analogous to that for $31(2^{11}\text{propervention})$ thiophene (6) with 1-bromopropane replaced by ethyl iodide. Purification by silica gel column chromatography eluted by petroleum ether/ethyl acetate (30:1, v/v) to furnish the pure product (yield, 47%). ¹H-NMR (500 MHz, CDCl₃), δ (ppm): 7.45 (dd, *J* = 0.80 Hz, 1 Hz, 1H), 7.25 (dd, *J* = 3.15 Hz, 3.00 Hz, 1H), 7.12 (dd, *J* = 0.95 Hz, 0.95 Hz, 1H), 4.34 (s, 2H), 3.64 (q, *J* = 7.05 Hz, 2H), 1.26 (t, *J* = 7.00 Hz, 3H). ¹³C-NMR (125 MHz, CDCl₃): 129.86, 128.99, 125.19, 121.68, 84.93, 81.02, 65.50, 58.50, 14.96. GC-MS: C₉H₁₀OS, [M]⁺ calc.: 166.05, found: 166.05 (M), 121.01 (M-C₂H₅O).

3-(3-Ethyoxylpropyl)thiophene (11). 3-(3-Ethyoxyl-1propynyl)thiophene (10, 3.54 g, 21.0 mmol), Pb/C (700.0 mg) and 20 mL of methanol was mixed in a high-pressure reactor. The reaction was then carried out at 60 °C under hydrogen with the pressure of 20 MPa for 48 h. Then the resulting mixture was filtered and the filtrate was concentrated using rotary evaporator. Pure product (3.08 g) was obtained from the crude residue after purification by silica gel column chromatography eluted by a mixture of ether/ethyl acetate (40:1, v/v) (yield, 86%). ¹H-NMR (500 MHz, CDCl₃), δ (ppm): 7.24 (dd, J = 3.35 Hz, 3.30 Hz, 1H), 6.94 (d, J = 4.40 Hz, 2H), 3.48 (q, J = 7.05 Hz, 2H), 3.43 (t, J = 6.45 Hz, 2H), 2.71 (t, J = 7.60 Hz, 2H), 1.90 (m, 2H), 1.21 (t, J = 7.00 Hz, 3H). ¹³C-NMR (125 MHz, CDCl₃), δ (ppm): 142.28, 128.21, 125.15, 120.05, 69.74, 66.09, 30.50, 26.76, 15.20. GC-MS: C₉H₁₄OS, [M]⁺ calc.: 170.07, found: 170.18 (M), 97.06 (M-CH₃CH₂OCH₂CH₂).

2-Bromo-3-(3-ethyoxylpropyl)thiophene (12). Similar to the preparation of 2-bromo-3-methylthiophene (**2**), the compound was prepared from 3-(3-ethyoxylpropyl)thiophene (**11**). The pure product was obtained by distilling the crude product under reduced pressure (yield, 67%). ¹H-NMR (500 MHz, CDCl₃), δ (ppm): 7.18 (d, *J* = 5.60 Hz, 1H), 6.80 (d, *J* = 5.55 Hz, 1H), 3.47 (q, *J* = 7.10 Hz, 2H), 3.42 (t, *J* = 6.48 Hz, 2H), 2.66 (t, *J* = 7.58 Hz, 2H), 1.86 (m, 2H), 1.21 (t, *J* = 7.00 Hz, 3H). ¹³C-NMR (125 MHz, CDCl₃), δ (ppm): 141.12, 128.26, 125.24, 109.10, 69.49, 66.12, 29.64, 25.98, 15.20. GC-MS: C₉H₁₃OSBr, [M]⁺ calc.: 247.99, found: 247.94 (M), 201.93 (M-C₂H₅O), 174.82 (M-CH₃CH₂OCH₂CH₂).

3-(4-Methoxyl-1-butyne)thiophene (14). Similar to the preparation of 3-(2-propoxyethyl)thiophene (6), the compound was prepared from 4-(3-thienyl)-3-butyne-1-ol (**13**). The pure product was obtained by silica gel column chromatography by using the eluent of the mixture of petroleum and ethyl acetate (40:1, v/v) (yield, 75%). ¹H-NMR (500 MHz, CDCl₃), δ (ppm): 7.37 (d, *J* = 2.10 Hz, 1H), 7.22 (dd, *J* = 3.00 Hz, 3.05 Hz, 1H), 7.08 (dd, *J* = 0.8 Hz, 0.8 Hz, 1H), 3.58 (t, *J* = 6.95 Hz, 2H), 3.4 (s, 3H), 2.67 (t, *J* = 6.95 Hz, 2H). ¹³C-NMR (125 MHz, CDCl₃), δ (ppm): 129.95, 127.98, 124.94, 122.52, 86.17, 76.46, 70.79, 58.68, 20.58, 14.16. GC-MS: C₉H₁₀OS, [M]⁺ calc.: 166.04, found: 151.21 (M-CH₃).

3-(4-Methoxylbutyl)thiophene (15). Similar to the preparation of 3-(3-ethyoxylpropyl)-thiophene **(11)**, the compound was prepared from 3-(4-methoxyl-1-butyne)thiophene **(14)** and purified by silica gel column chromatography by using the eluent of the mixture of petroleum and ethyl acetate (40:1, v/v) (yield, 86%). ¹H-NMR (500 MHz, CDCl₃), δ (ppm): 7.23 (dd, *J* = 3.05 Hz, 3.05 Hz, 1H), 6.93 (d, *J* = 4.85 Hz, 2H), 3.39 (t, *J* = 6.38

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Hz, 2H), 3.32 (s, 3H), 2.65 (t, J = 7.50 Hz, 2H), 1.69 (m, 2H), 1.62 (m, 2H). 13 C-NMR (125 MHz, CDCl₃), δ (ppm): 142.70, 128.16, 125.10, 119.93, 72.57, 58.51, 30.02, 29.25, 27.06. GC-MS: C₉H₁₄OS, [M]⁺ calc.: 170.08, found: 170.12 (M), 110.04 (M-CH₃OCH₂CH₂).

2-Bromo-3-(4-methoxylbutyl)thiophene (16). Similar to the preparation of 2-bromo-3-methylthiophene (**2**), the compound was prepared from 3-(4-methoxylbutyl)thiophene (**15**) and purified by distillation under reduced pressure with a yield of 73%. ¹H-NMR (500 MHz, CDCl₃), δ (ppm): 7.18 (d, *J* = 5.60 Hz, 1H), 6.80 (d, *J* = 5.60 Hz, 1H), 3.39 (t, *J* = 6.13 Hz, 2H), 3.32 (s, 3H), 2.60 (t, *J* = 7.25 Hz, 2H), 1.63 (m, 4H). ¹³C-NMR (125 MHz, CDCl₃), δ (ppm): 141.48, 128.15, 125.24, 109.98, 72.48, 58.56, 29.12, 29.11, 26.30. GC-MS: C₉H₁₄OSBr, [M]⁺ calc.: 247.99, found: 247.92 (M), 168.93 (M-Br), 136.91(M-Br-CH₃O).

Synthesis of polymers. A general procedure for polymerizations described below.57 To a solution of 2-bromo-3is (butoxymethyl)thiophene (4) (6.25 g, 25.2 mmol) in 100 mL of anhydrous THF was added dropwise with 12.5 mL of 2 M LDA (25.0 mmol) in anhydrous THF at -78 °C under nitrogen. After stirring for 1 h at -78 °C, a solution of anhydrous ZnCl₂ (4.90 g, 36.0 mmol) in 100 mL of anhydrous THF was transferred in. The reaction mixture was stirred for an additional hour at -78 °C and then warmed to room temperature. Ni(dppp)Cl₂ (136.0 mg, 0.25 mmol, 1% equiv.) was then added in and the reaction was kept at room temperature overnight to yield a thick viscous solution. After the partial removal of the solvent by rotavap, the mixture was precipitated into 200 mL of methanol and filtered. The crude product was transferred into a Soxhlet thimble and sequentially with methanol, extracted hexanes. and chloroform. The chloroform extraction was then concentrated and dried in vacuum to furnish 2.20 g of the final polymer product poly(3-(butoxymethyl)thiophene).

Poly(3-(butoxymethyl)thiophene) (**P3BOMT**, yield, 50%). ¹H-NMR (500 MHz, CDCl₃), δ (ppm): 7.24 (s, 1H), 4.58 (s, 2H), 3.58 (t, J = 6.30 Hz, 2H), 1.64 (m, 2H), 1.45 (m, 2H), 0.96 (t, J = 7.00 Hz, 3H). M_n = 9.0 kg mol⁻¹, M_w = 19.1 kg mol⁻¹, PDI = 2.13.

Poly(3-(2-propoxyethyl)thiophene) (**P3POET**, yield, 57%). ¹H-NMR (500 MHz, CDCl₃), δ (ppm): 7.10 (s, 1H), 3.72 (t, *J* = 6.90 Hz, 2H), 3.46 (t, *J* = 6.60 Hz, 2H), 3.31 (t, *J* = 6.65 Hz, 2H), 1.64 (q, *J* = 7.05 Hz, 2H), 0.95 (t, *J* = 7.40 Hz, 3H). M_n = 7.2 kg mol⁻¹, M_w = 10.9 kg mol⁻¹, PDI = 1.51.

Poly(3-(3-ethoxypropyl)thiophene) (**P3EOPT**, yield, 36%). ¹H-NMR (500 MHz, CDCl₃), δ (ppm):7.02 (s, 1H), 3.50 (dt, 4H), 2.90 (t, *J* = 7.50 Hz, 2H), 1.98 (m, 2H), 1.22 (t, *J* = 6.95 Hz, 3H). M_n= 12.4 kg mol⁻¹, M_w = 15.7 kg mol⁻¹, PDI = 1.26.

Poly(3-(4-methoxybutyl)thiophene) (**P3MOBT**, yield, 50%). ¹H-NMR (500 MHz, CDCl₃), δ (ppm): 6.99 (s, 1H), 3.44 (t, *J* = 6.35 Hz, 2H), 3.35 (s, 3H), 2.84 (t, *J* = 7.10 Hz, 2H), 1.77 (m, 2H), 1.73 (m, 2H). M_n = 13.2 kg mol⁻¹, M_w = 17.9 kg mol⁻¹, PDI = 1.36.

2.3 Polymer films for thermoelectric performance measurements

Glass substrates with the size of 2 cm \times 2 cm were sonicated in acetone, isopropanol, ethanol and deionized water sequentially and washed by the corresponding solvent and dried by a flow of

nitrogen. The substrates were then transferred to an UVOCS ultra-violet ozone cleaning system and exposed to 00 vozone for 10 min prior to use. The polymers were dissolved in chlorobenzene (CB) respectively with concentration as 30 mg mL⁻¹. Then polymer films were spin-coated on the glass substrates at 1000 rpm for 1 min and dried naturally under ambient condition to offer film thickness around ~200 ± 40 nm. Anhydrous FeCl₃ was dissolved in nitromethane with the concentration of 0.01M. The polymer films were then immersed in FeCl₃ solutions for certain periods of time, rinsed by nitromethane, and subsequently dried by an air flow before being transferred instantly to a measurement system of ULVAC-RIKO ZEM-3 (Ulvac, Japan) at ambient temperature under helium atmosphere. The air humidity was controlled at 30% ~ 40%.

3. Results and Discussion

3.1 Synthesis and characterization of P3HT analogues

The molecular structures of all P3HT analogues and their synthetic routes are depicted in Scheme 1. The standard procedure of the Rieke polymerization method was employed to prepare the polymers due to its strong capability of achieving high regioregularity of P3HT with desired Mn and low PDI values.⁵⁷⁻⁵⁹ The molecular weights of the polymers determined by gel permeation chromatography (GPC) were found to be in the range of 7.2 - 13.2 kg mol⁻¹ with PDIs in the range of 1.2 - 1.5 except around 2.13 for P3BOMT. ¹H-NMR spectroscopy of the polymers provided unequivocal evidence for the introduction of oxygen atoms at the specific positions along the side chain. The regioregularity of the polymers is typically calculated by comparing the integrated peaks corresponding to the α methylene protons to thiophene unit on the side chains in headto-tail (HT) versus head-to-head (HH) linkages. In particular, δ 4.42 for P3BOMT, δ 2.85 for P3POET, δ 2.65 for P3EOPT, δ 2.59 for P3MOBT, δ 2.56 for P3HT (Fig. S1 - S5). This gives 70%, 96%, 95%, 97%, and 95% HT percentage for P3BOMT, P3POET, P3EOPT, P3MOBT, and P3HT respectively. The much lower regioregularity (70%) and higher PDI value of P3BOMT relative to the other polymers could be ascribed to more unbalanced reactivity of 2- and 5- position of thiophene unit caused by the electron-withdrawing oxygen atom at the β position, which probably increases the content of non-HT linkages in the polymer. The strength of such electron-withdrawing inductive effect of the strong electronegative oxygen atom on thiophene units becomes weaker and weaker when oxygen atom is moving beyond the β position. Much higher HT regioregularities and uniform PDIs were reasonably achieved for the other three polymers, which are comparable to that of the commercial P3HT. The decomposition temperatures T_{d} for polymers are determined by 5% weight loss, 296, 330, 369, 404, and 450 °C for P3BOMT, P3POET, P3EOPT, P3MOBT and P3HT, respectively (Fig. S6).

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3.2 Melting and crystallization behaviors

The effects of sequential oxygen substitution along the alky side chain from the β to the ω position on the melting and crystallization behaviors of P3HT analogues were investigated by differential scanning calorimeter (DSC) measurements. The heating and cooling thermograms of the second cycle of the polymers are presented in Fig. S7. For P3BOMT, no melting and crystallization peak can be clearly detected, which could be ascribed to its much lower HT regioregularity around 70%. In the heating cycle, P3HT offered the highest peak melting temperature (T_m) of 222 °C, which is in great agreement with the reported T_m values.⁶⁰ The peak T_m values of P3POET, P3EOPT, and P3MOBT were determined to be 177, 200, and 211 °C, respectively, apparently indicating a progressively increasing trend when oxygen atom moves towards the end of the side chain. The second cooling scans indicate apparent propensity of crystallization for the polymers of P3POET, P3EOPT, P3MOBT, and P3HT. A similar shift of the crystallization temperatures (T_c) towards higher temperatures can be observed as well. The peak T_c values of P3POET, P3EOPT, P3MOBT, and P3HT were found to increase from 117, 148, 174 to 187 °C. A broad crystallization process can be noticed for P3POET. Although P3BOMT doesn't present obvious melting and crystallization behavior, the increasing trends in the T_m and T_c values indicate that the thermal property of the P3HT can be effectively controlled by engineering the position of O atom located at the side chain, suggesting the existence of varied intermolecular interaction among the polymers in solid state.



Fig. 1 The melting temperature (T_m) and crystallization temperature (T_c) of the polymers as a function of the position of O atom along the side chain.

3.3 Optical and electrochemical properties

The solution $(1.0 \times 10^{-5} \text{ g mL}^{-1}$ in chlorobenzene) and thin-film UV-vis absorption spectra of all polymers at room temperature are depicted in **Fig. 2**. In diluted chlorobenzene solution, all the polymers show a single absorption band with slightly varied maximum wavelength ($\lambda_{max,sol}$) around 456 nm as tabulated in **Table 1**, which originates from $\pi - \pi^*$ transitions on the conjugated backbones. The extinction coefficients (ε_{sol}) of these bands range from 2.5×10^4 to 3.5×10^4 mL cm⁻¹ g⁻¹, as compiled in **Table 1**. When going from the solution to the thin film state, the peak from the $\pi - \pi^*$ transitions is red-shifted around 58 nm for P3POET, P3EOPT, P3MOBT and P3HT, while it is only around 25 nm for P3BOMT. It should be noted that the formation of vibronic shoulders at the lower energy area can be obviously observed for all the polymers except for P3BOMT. This is

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especially the case for P3POET with the O atom located at the γ position in the side chain, implying an increased intermolecular interaction and ordering in the film over the others. The maximum wavelengths of films ($\lambda_{max,film}$) and the corresponding absorption coefficients (ε_{film}) are presented in **Table 1** as well. In addition, except for P3BOMT with an optical bandgap (Eg) of 2.11 eV, the other four polymers yield similar band gaps of around Eg = 1.92 eV.



Fig. 2 UV-vis absorption spectra of the polymers in PhCl solutions at 1.0×10^{-5} g mL⁻¹ (a) and in films as casted from the corresponding PhCl solutions at 30 mg mL⁻¹ (b).

The electrochemical properties were further investigated by cyclic voltammetry to figure out the energy level of HOMO and LUMO of all the polymers (**Fig. S8**). Irreversible oxidative responses were observed. The HOMO energy levels (E_{HOMO}) at - 5.36, -5.24, -5.15, -5.10, and -5.21 eV were calculated from the oxidation onset potentials (E_{ox}^{onset}) as presented in **Table 1** for P3BOMT, P3POET, P3EOPT, P3MOBT and P3HT, respectively. The O-substituted polymers roughly exhibit a tendency to be **Table 1**. Summary of the photophysical and electrochemical properties of all polymers.

more easily oxidized when the O atom is moved from the $\beta_{\rm m}$ to the ω position along the side chain. This Can be well explained by the electron-withdrawing inductive effect of O atom. When the O atom moves outwards from the β to the ω position, its electron-withdrawing inductive effect decreases. The conjugated backbone becomes relatively more electron-rich and tends to be more easily oxidized to offer a lower $E_{\rm ox}^{\rm onset}$. The apparent effect of such side chain engineering on redox properties of the resulting conjugated polymers was seldom observed. The LUMO energy levels of the polymers were estimated to range from -3.2 to -3.3 eV according to the equation of $E_{\rm LUMO} = (E_{\rm HOMO} + E_g)$.

With much lower regioregularity, the UV-vis absorption spectra of P3BOMT both in solution and in film differ greatly from the others. Moreover, the HOMO level of P3BOMT is much deeper due to the existence of electron-withdrawing inductive effect of the β oxygen atom on the conjugated backbone. In order to objectively explore the effect of oxygen substitution on solid-state ordering and thermoelectric performance, P3BOMT is therefore excluded from the other P3HT analogues in following investigations. On the other hand, the variation of molecular weight was also noticed among P3POET, P3EOPT, P3MOBT and P3HT with comparable regioregularities. Effective conjugation length (n_{ECL}) is an important point from which further extension of the conjugated chain does not affect a certain property any more, for example, the maxmium absorption wavelength and the band gap in the solid state. For polythiophenes, the effective conjugation length was proven to be 20 ~ 22 monomers.^{61, 62} Here, the effective conjugation length is around 42 monomers for P3POET with the lowest Mn, which is quite enough for the saturation of photophysical properties. As can be proven by the absorption spectra depicted in Fig. 2, the maxmium absorption wavelength of P3POET, P3EOPT, P3MOBT and P3HT both in solution and in film are consistent with each other. The effect of molecular weight was therefore not taken into consideration for the study on solid state ordering and OTE below.

Polymer	$\lambda_{ ext{max,sol}}$ (nm)	€ _{sol} (mL cm ⁻¹ g ⁻¹)	$\lambda_{\sf max, film}$ (nm)	$arepsilon_{ m film}$ (10 ⁴ cm ⁻¹)	E _g (eV)	E _{ox} ^{onset} (V)	Е _{номо} (eV)	E _{LUMO} (eV)
P3HT	460	3.5×10^{4}	515, 551, 603	7.0, 6.1, 3.1	1.92	0.51	-5.21	-3.29
P3BOMT	452	3.2×10^{4}	476	6.5	2.11	0.66	-5.36	-3.25
P3POET	455	2.7×10^{4}	520, 556, 608	8.4, 8.4, 6.1	1.92	0.54	-5.24	-3.32
P3EOPT	460	2.5×10^{4}	513, 545, 600	5.8, 5.4, 2.8	1.94	0.45	-5.15	-3.21
P3MOBT	458	$3.3 imes 10^4$	518, 551, 603	6.8, 6.4, 4.1	1.92	0.40	-5.10	-3.18

3.4 Solid state ordering of neutral polymers

Powder X-ray diffraction measurements were performed to gain insight into the structural ordering of the pure polymers in solid state. As shown in **Fig. S9**, a diffraction peak at 20 of 5.30, 5.60, 5.78 and 5.85° can be observed for P3HT, P3POET, P3EOPT and P3MOBT, respectively, corresponding to distance value (d)

of 16.66 Å, 15.77 Å, 15.28 Å, and 15.10 Å, respectively, determined by the interchain stacking of corresponding side chains. It is obvious that the stacking between the side chains becomes more compact from P3HT and P3POET to P3MOBT. A diffraction peak at 2 θ around 24.08° can be noticed for P3POET, corresponding to typical backbone π - π stacking distances of 3.69 Å. A similar diffraction peak at 2 θ around 23.41° with

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relatively larger π - π stacking distance of 3.80 Å can be observed as well for the other three polymers. Moreover, P3POET shows comparably high and sharp peaks to P3HT, indicating better crystallinity over the other polymers with Osubstitution in side chains. Grazing incident wide-angle X-ray scattering (GIWAXS) was employed as well to probe the molecular packing in polymer films under neutral state and polymer orientations of crystalline lamellae with respect to the silicon substrate. As shown in Fig. S10, all polymers films exhibit preferable edge-on orientated molecular packing. Lamellar diffractions in the out-of-plane (OOP) direction determined by side chain interactions can be observed at q_z around 0.39, 0.40, 0.42 and 0.43 Å⁻¹ (*d* =16.10, 15.70, 14.95 and 14.60 Å accordingly) accompanied with a π - π stacking peak in the inplane (IP) direction at q_r around 1.68, 1.70, 1.64 and 1.64 Å⁻¹ (d = 3.74, 3.69, 3.83 and 3.83Å accordingly) for P3HT, P3POET, P3EOPT and P3MOBT respectively, which is in excellent agreement with powder XRD results. The lamellar stacking distance shrinks while the π - π stacking distance expands when substituting carbon atoms from the γ to the ω position with O atom. Interestingly, P3POET almost displays the longest edgeon oriented lamellar stacking distance and the shortest π - π stacking distance among all O-substituted polymers. The evolution of the lamellar stacking distance of the polymer films is directly correlated with the location of the O atom in the side alkyl chains with the according ending propoxyl, ethyoxyl and methoxyl groups. Siegel et al. once reported more favourable sandwich π - π stacking of aryl rings with electron-withdrawing substituents reducing the electron density of aryl rings.⁶³ In this work, the existence of the γ -positioned O atom leads to a relatively more electron-deficient conjugated backbone for P3POET. The closer π - π stacking existed in the P3POET film could be explained similarly in comparison with the other two O-containing polymers. Moreover, the crystallinity of edge-on oriented P3POET is overwhelmingly higher than the crystallinity of any other O-substituted polymers, even that of P3HT, which agrees well with the film absorption feature as indicated in Fig. 2. From the in-plane GIWAXS profiles shown in Fig. S10, partial face-on orientation can be noticed for the polymers except P3MOBT without obviously detectable coexistence of face-on orientated crystals. Moreover, the face-on orientated lamellar stacking peak of P3POET is much weaker and broader than those of P3EOPT and P3HT, suggesting much inferior polymer crystallinity in this orientation.

3.5 Thermoelectric properties

To evaluate the thermoelectric properties of the films of these P3HT analogues with such O-substitution on side chains, the electrical conductivity and Seebeck coefficient were measured

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in a He-filled chamber with the four-probe configuration at room temperature. The films were doped by it meres ing the films the oxidant solutions of FeCl₃ in nitromethane at varied concentrations over various doping time prior to the measurements. The optimized concentration of the FeCl₃ solution was found to be 0.01 mol L⁻¹, which resulted in easily measurable electrical conductivities for all polymers (Table S1). Polarons and bipolarons have been proposed as the dominant charge carriers in a conjugated polymer at a certain doping level. Electronic transitions associated with positive polarons and bipolarons appear below the band edge of the polymer in the visible, near-infrared (NIR), and even middle infrared regions (MIR), which can be experimentally distinguished by the number of strong absorption bands.^{64, 65} In particular, a polaron exhibits strong two-band feature while a bipolaron exhibits a strong one-band feature at longer wavelength. Due to the difficulty of determining the charge carrier density, it would be very helpful to consider how the absorption of the neutral polymer films evolves upon doping. Thus, before the discussion of the thermoelectric property of the respective doped polymer films, optical absorption spectroscopy was utilized to determine the nature of charge carriers in films with different doping levels achieved by immersing them in a 0.01 mol L⁻¹ solution of FeCl₃ in nitromethane for different time durations (Fig. 3). For the P3POET film, the π - π * transition in the neutral film at 520 nm is found to continuously decrease with the prolonged doping time, and is accompanied by a simultaneous appearance of absorption bands at 780 nm (1.82 eV) and above 1500 nm. The absorption intensity of the band at 780 nm reaches the maximum after doping for 2 min. A slight decrease of the absorption at 780 nm and a continuous increase above 1500 nm can be then observed after further doping, leading to the formation of two isosbestic points at around 630 and 930 nm, indicating the formation of positive bipolarons from positive polarons after doping for 2 min. P3EOPT presents a doping time dependent absorption feature with two-band absorption and a single isosbestic point at around 620 nm, indicating that only polarons formed within 60 min. P3MOBT exhibits a similar doping-induced two-band absorption feature as that of the film of P3POET with two isosbestic points, while the formation of bipolarons starts after doping for 20 min. The time dependent doping absorption spectrum of the P3HT film was also recorded as a reference. A similar two-band absorption feature to that of P3POET was observed including two isosbestic points at 620 and 910 nm, and the formation of bipolarons started after doping for 2 min. Briefly, only positive polarons formed after doping for within 60 min for the film of P3EOPT, whereas positive bipolarons started to form from positive polarons after doping P3POET and P3HT for 2 min and P3MOBT for 20 min.

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Fig. 3 UV-vis-NIR absorption spectra of polymer films doped at various doping levels by immersing the films in 0.01 mol L-1 solution of FeCl₃ in nitromethane at r.t. over different times.

Raman spectra analysis was also carried out to investigate the effect of FeCl₃ doping on the structure characteristics of polymer films. Raman spectra of the films excited at 514 nm were obtained before and after doping for within 30 min as presented in Fig. S11. The bands at ~1380 cm⁻¹ (C_{β} - C_{β} stretching vibration) and at ~1450 cm⁻¹ ($C_{\alpha} = C_{\beta}$ stretching vibration) are observed for the films of P3POET, P3EOPT, P3MOBT, and P3HT in neutral state.^{66, 67} Doping treatment have an unremarkable effect on the position of the Raman bands, but make the $C_{\alpha} = C_{\beta}$ stretching vibrations broader. The films of P3POET, P3MOBT and P3HT present a slight shift of the $C_{\alpha} = C_{\beta}$ stretching vibration towards higher frequency, revealing the transition of conjugated chains from benzoid to quinoid structure as the doping proceeds.^{68, 69} Such transitions suggest the appearance of bipolarons in agreement with the corresponding doping time dependent UV-vis-NIR absorption spectra.

Thermoelectric parameters of σ , S, and PF of all polymer films with different levels of doping are depicted in Fig. 4. For these polymer films, the electrical conductivities initially increase, to reach the maxima, and then decrease as the doping time increases. The doping time corresponding to the highest

electrical conductivity varies from polymer to polymer. The P3HT film present its highest electrical conductivity of 246.1 S cm⁻¹ after immersion for 10 min, at which time both polarons and bipolarons exist in the film of P3HT. For the P3POET and P3MOBT films, the highest electrical conductivity of 193.5 and 223.1 S cm⁻¹, respectively, was attained after immersion in the oxidation solution for 40 seconds, with the charge carrier in the form of polarons. The P3EOPT film gives the highest electrical conductivity as 250 S cm⁻¹ after immersion for 2 min, with polarons as the only charge carrier. The Seebeck coefficient of P3HT film presents a continuously decreasing magnitude right from the beginning, while the other three films exhibit an initial increase in the Seebeck coefficient, reach a maximum, and then decrease as the doping time increases. The largest Seebeck coefficients are determined to be 34.0, 22.3, 26.3 and 61.5 μ V K⁻¹ with the doping time of 120, 120, 120 and 20 seconds for P3EOPT, P3MOBT, and P3HT, respectively. P3POET, Interestingly, relatively high S values can only be attained in the early doping state, for immersion times of less than 10 min for all polymers.

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Fig. 4 Electrical conductivities (in orange color) and Seebeck coefficients (in gray color) of (a) P3HT, (b) P3POET, (c) P3EOPT and (d) P3MOBT. Critical points of the doping time resulting in the initial formation of positive bipolarons from positive polarons are indicated by the dotted cyan lines.

Despite differences in the electrical conductivities and Seebeck coefficients among all polymers, the integrated response of the electrical conductivity and the Seebeck coefficient to the doping time leads to an increase of the power factors that reach their own maxima before falling at longer immersion times (**Fig. 5**). Due to the fact that the Seebeck coefficient and the electrical conductivity of the P3POET film are both high at low doping levels, the *PF* of the film achieved almost a factor of two higher value of 19 μ W m⁻¹ K⁻² after doping for 40 seconds than any other film. For the films of P3EOPT and P3MOBT, the maximum *PF* values were around 12.5 and 11.5 μ W m⁻¹ K⁻², respectively. The reference P3HT film yielded a maximum *PF* around 11.7 μ W m⁻¹ K⁻². It is worthwhile to note that all these maximum *PF* values were obtained in a state of doping characterized by the dominance of polarons.



3.6 Solid state ordering of doped polymer films with optimized PFs

GIWAXS measurements were performed again as indicated in Fig. 6 to examine changes in the local molecular organization of the films doped analogously by immersion in a solution of FeCl₃ in nitromethane over the time that gave the optimized *PFs*, namely 40 seconds for P3POET and P3MOBT, and 2 min for P3HT and P3EOPT. All doped polymers formed semi-crystalline films with strong texturing. The scattering patterns were broadened slightly and the conformation of preferentially edgeon orientated crystalline lamellae remained upon doping. The OOP (100) lamellae distances (~16.10 Å) became very close

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among all polymers except for P3MOBT (~15.32 Å), while the IP (010) π - π stacking distances were almost similar (~3.81 Å), except for P3POET (~3.71 Å, remaining the shortest). Meanwhile, the crystallinity of OOP (100) lamellae diffractions were improved greatly for doped P3MOBT and P3POET, which were much weaker in their undoped form. A significant change is that the crystallinity of the face-on oriented crystalline lamellae was strengthened for P3EOPT, P3MOBT and P3HT compared with their undoped films (Fig. S10), with the obvious appearance of OOP (010) diffractions at the q_z around 1.65 Å⁻¹ (with d space ~3.81 Å) corresponding to vertical π - π stacking. Evolution of the film structure with varied doping levels has been observed in quite a few solution doping examples due to the incorporation of counterion from the dopants, depending on chemical structure of the materials and the doping level.^{38,} ^{70, 71} Overall, the changes of in-plane scattering features are quite similar in P3EOPT, P3MOBT and P3HT polymer films, but not in P3POET, which shows the strongest crystallinity of the edge-on orientated crystal lamellae (out-of-plane scattering) after immersion doping for 40 seconds. Moreover, the crystallinity of the face-on orientated crystal lamellaes (in-plane scattering) of P3POET was the weakest with barely detectable OOP (010) π - π stacking diffraction. It seems that the local

structure order of the P3POET film was not disturbed much after doping for 40 seconds. Meanwhile, doping/with Fech makes molecular packing in the three polymer films of P3EOPT, P3MOBT and P3HT comparable and eliminates the differences observed in their molecular packing states when undoped. Practically, the maximum electrical conductivities for all polymers are fairly close and in the range of 200 - 250 S cm⁻¹ although they were achieved at different doping times. The attainable similar highest electrical conductivities of all films could be attributed to their retention of the preferred edge-on orientation, which facilitates the in-plane charge transport after doping at a certain level. However, at the immersion doping time corresponding to the maximum PF for each polymer, only the doped P3POET film maintains both S and σ relatively high and close to the maximum values, while the other polymers yield either high S but much lower σ (P3HT) or high σ but much lower S (P3EOPT and P3MOBT) as shown in Fig. 4. The square dependence of PF on S together with higher σ amplifies the difference on the PF of P3POET from the other polymers. The dominant edge-on orientation with stronger crystallinity and closer edge-on oriented π - π stacking might be responsible for the higher integrated PF observed in this polymer at an appropriate doping level.



Fig. 6 GIWAXS profiles (a) and patterns (b) along out-of-plane (OOP) and in-plane (IP) directions of all polymer films on Si substrate immersed in 0.01M FeCl₃/CH₃NO₂ solution for the doping time corresponding to the maximum power factor (P3HT: 2 min, P3POET: 40 seconds, P3EOPT: 2 min and P3MOBT: 40 seconds).

4. Conclusions

Due to the existence of the shorter bond length and the smaller rotation energy of the CH₂-O bond than the CH₂-CH₂ bond, sequential O-substitution carbon atoms from the γ position outwards along the hexyl side chains of RR-P3HT to the ω position led to the increase of the melting and the crystallization temperature of the resultant polymers. The neutral polymer films feature decreased edge-on oriented lamellar stacking distance and increased π - π stacking distance. UV-vis-NIR spectroscopy confirmed the presence of polarons and/or the combination of polarons with bipolarons by probing their

characteristic absorptions upon increasing the immersiondoping time in a FeCl₃ solution in nitromethane at room temperature. The similar highest electrical conductivities of all doped films were attained. Morphology studies of polymer films with optimized doping time corresponding to the maximum *PFs* revealed that all the polymers favored the formation of edge-on orientated molecular packing with respect to the substrate. Moreover, the polymer with the γ Osubstitution exhibited the largest proportion and the strongest crystallinity of edge-on oriented lamellas with the closest $\pi - \pi$ stacking. The attractive molecular packing state of the polymer enabled its maintenance of both *S* and σ close to their maximum values, resulting in the optimized *PF* almost two times of the

polymers with O-substitution on the δ and ω positions with high σ unfavorably coupled with lower *S*. Although how σ coupled with *S* responds to polymer film morphology evolution is not clear, this research successfully demonstrates a facile strategy on fine-tuning the solid-state organization and polymer thermoelectric properties via side-chain engineering of semiconducting polymers by sequential oxygen-substitution on carbon atoms. This attractive approach could assist in establishing the guidance for further structure optimization toward high performance polymer-based thermoelectric materials.

Conflicts of interest

There are no conflicts to declare.

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Sequential O-substitution along alkyl side chain of regioregular P3HT analogues

fine-tunes their film microstructure and thermoelectric property.

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