Electronic Supplementary Information (ESI)

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

Liangjun Chen,^a Wei Liu,^a Yonggao Yan,^a Xianli Su,^a Shengqiang Xiao,^{*,a} Xinhui Lu,^{*,b} Ctirad Uher^c and Xinfeng Tang^{*,a}

^a State Key Laboratory of Advanced Technology for Materials Synthesis and

Processing, Wuhan University of Technology, Wuhan 430070, China

^b Department of Physics, Chinese University of Hong Kong, Hong Kong, P. R. China

^c Department of Physics, University of Michigan, Ann Arbor, MI 48109, USA

* Corresponding Emails:

shengqiang@whut.edu.cn, xhlu@phy.cuhk.edu.hk, tangxf@whut.edu.cn

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1. Experimental details on measurements and instrumentation.

All ¹H- and ¹³C-NMR spectra were recorded on a Bruker Advance III-HD-500 MHz spectrometer in deuterated chloroform at 298 K. The chemical shifts (δ) are reported in parts per million (ppm). ¹H-NMR chemical shifts were referenced to tetramethylsilane (TMS, 0.00 ppm), and ¹³C-NMR chemical shifts were referenced to deuterated chloroform (CDCl₃, 77.00 ppm). The thermogravimetry analysis was carried out on a NETZSCH syncthermogravimetric analyzer (STA449F3) at a heating rate of 10 °C min⁻¹ under nitrogen, and the temperature of degradation (T_d) was correlated to a 5% weight loss. A differential scanning calorimetry (DSC) apparatus (Q20, Thermal Analysis, USA) was used to characterize the melting and crystallization properties of polymers.

UV-vis absorption spectra of the films spin-coated on the precleaned glass were taken on a Shimadzu UV-1750 spectrophotometer. UV-vis-NIR absorption spectra of doped and undoped films were obtained on a Lambda 750 S spectrophotometer. Raman spectra were obtained with a Renishaw inVia Raman Microscope mounted with a Leica N Plan 50×/0.75 EPI objective lens by using a 514 nm laser. Powder XRD patterns were obtained by utilizing a PANalytical X'Pert diffractometer. Grazing incident wide angle X-ray scattering (GIWAXS) analysis was carried out for undoped polymer films at BL23A SWAXS beamline of a superconductor wiggler at the National Synchrotron Radiation Research Center, Hsinchu, Taiwan, using 10 keV beam incident at 0.15°, a C9728DK area detector and a Pilatus detector. The GIWAXS measurement on doped films was carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incidence angle was 0.2°. Polymers were spin-coated from the solutions in chlorobenzene on precleaned silicon substrates with spin-coater (WS-650MZ-23NPP) in a glovebox and left to dry naturally before GIWAXS analysis. The thickness of films was measured on a DEKTAK XT profilometer. The electrical conductivity and Seebeck coefficient of films were measured simultaneously by a four-point probe method under Helium atmosphere utilizing a commercial system of ULVAC-RIKO ZEM-3 apparatus. For the Seebeck coefficient measurement, a temperature difference was created at the two ends of sample by resistance heating at one end, which generates the thermoelectric voltage (ΔV) between two probes with temperature gradient of ΔT . The Seebeck coefficient is then calculated by $\alpha = \Delta V / \Delta T$.

Cyclic voltammogram (CV) measurements were obtained in a solution of 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in anhydrous acetonitrile as the supporting electrolyte on a CHI 605E electrochemical analyzer using a standard three-electrode configuration, with a glassy carbon disk electrode as the working electrode, a platinum wire as the counter electrode and an Ag/AgNO₃ (0.01M AgNO₃ in the supporting electrolyte) electrode as the reference electrode. The measurements of the polymer film drop-casted on the working electrode from a 3 mg mL⁻¹ solution in CHCl₃ were done at a constant scan rate of 100 mVs⁻¹ at room temperature under highly purified N₂.

2. ¹H-NMR spectra of the polymers in this work.



Fig. S1 ¹H-NMR spectrum of P3BOMT















Fig. S5 ¹H-NMR spectrum of P3HT

3. Supplementary figures.



Fig. S6 Thermogravimetric curves of P3HT analogues



Fig. S7 The second cycle DSC heating (a) and cooling (b) curves of the P3HT analogues at a rate of 10 °C min⁻¹.



Fig. S8 Cyclic voltammogram curves of P3HT analogues (Scanning speed: 100 mVs⁻¹; Electrolyte: 0.1 mol L⁻¹ Bu₄NPF₆ in anhydrous acetonitrile)



Fig. S9 Powder XRD patterns of P3HT analogues



Fig. S10 (a) In-plane and out-of-plane GIWAXS profiles of the films of neutral polymers on silicon substrate, and (b) their corresponding diffraction patterns.

Table S1. Summary of the optimized thermoelectric performance at different concentrations of FeCl₃/CH₃NO₂ solution (results shown below are the mean values of three measurements).

Concentration of	Polymer	$\sigma_{\rm max}$	S _{max}	PF_{max}
FeCl ₃ in CH ₃ NO ₂		$(S \text{ cm}^{-1})$	$(\mu V K^{-1})$	$(\mu W m^{-1} K^{-2})$
0.005M	P3POET	99	57	14
	P3EOPT	93	47	8.3
	P3MOBT	71	42	8.6
	РЗНТ	97	83	8.3
0.01M	P3POET	193.5	34	19
	P3EOPT	250	22.3	12.5
	P3MOBT	223.1	26.3	11.5
	РЗНТ	246.1	61.5	11.7
0.02M	P3POET	109	22.7	4.8
	P3EOPT	102	18.7	3.4
	P3MOBT	119	21.7	5.6
	РЗНТ	122	30	8.6



Fig. S11 Doping time dependent Raman spectra of the P3HT analogues