Electronic Supporting Information

Synthesis and Brønsted acid doping of solution processable poly(thienylene vinylene) for thermoelectric application

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General Experimental Section

Materials. Tetrahydrofuran (THF, 99.5%, stabilizer free, Kanto Chemical Co., Inc.) was refluxed over sodium benzophenone under nitrogen for 2 h, then distilled just before use. (3,4-Bis(2-ethylhexyl)-5-formyl-thiophene-2-ylmethyl)phosphonic acid diethyl ester (1a) was synthesized modifing a previously reported procedure.¹ All other reagents were purchased from Sigma-Aldrich Japan K.K., Tokyo Chemical Industry (TCI) Co., Ltd., Kanto Chemical Co., Inc. or FUJIFILM Wako Pure Chemical Industries, Ltd., and used as received.

Characterizations. ¹H and ¹³C nuclear magnetic resonance (¹H NMR and ¹³C NMR) spectra for the polymer characterization and the determination of chain-end functionality were recorded on a JEOL JNM-ECX400 (400 MHz) in deuterated chloroform-*d* (CDCl₃) at 25 °C calibrated to chloroform as a standard (δ H 7.26). The number-average molecular weight (M_n), weightaverage molecular weight (M_w), and molar-mass dispersity (D_M) values were measured by size exclusion chromatography (SEC) using a JASCO GULLIVER HPLC system equipped with a pump (JASCO PU-4580), a column oven (JASCO CO-1565), a UV detector (UV, λ = 254 nm, JASCO UV-4575), and an RI detector (RI-4030). The column set was as follows: a guard column (Shodex K-G 4A) and two consecutive columns (Shodex K-804L, Shodex K-805L) eluted with THF at 40 °C at a flow rate of 1.0 mL min⁻¹. Polystyrene standards were employed for a calibration for SEC. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C/min for thermogravimetry analysis (TGA) and a TA Instruments Q-100 connected to a cooling system at a heating rate of 10 °C/min for differential scanning calorimetry (DSC).

UV-vis-NIR absorption spectra were measured by a spectrophotometer (U-4100, Hitachi). Room temperature electron paramagnetic resonance (EPR) spectra were collected at X-band frequency by EPR spectrometer (ELEXSYS-E580, Bruker). Work functions and the onset of valence band were determined by ultraviolet photoelectron spectroscopy (UPS) (PHI 5000 VersaProbe III, ULVAC-PHI. Inc.) with He I gas discharge line (21.2 eV); for the measurementes, the samples were biased at -5 V. The HOMO levels were measured by photoelectron spectroscopy in air (PESA) (AC-2 PESA spectrometer, Riken Keiki). ¹⁹F Nuclear magnetic resonance (NMR) spectra were measured using 400 MHz NMR spectrometer (AVIII-400, Bruker). Raman spectra were collected with a UV spectrometer (LabRAM HR800, Horiba Jobin Yvon) equipped with Nd:YAG laser (incident laser wavelength: 532 nm). The surface morphology was scanned under tapping mode by using atomic force microscopy (AFM5100N, Hitachi). Image capture and measurement of contact angle were performed at a contact angle meter (CAM110, Creating Nano Technology). 2D grazing-incidence wide-angle scattering (2D GIWAXS) measurements were performed at the National Synchrotron Radiation Research Center (NSRRC) of Taiwan on the beamline of TPS 25A.

Synthesis



Scheme S1. Synthesis of monomer precursor 1a.

Synthesis of 3,4-bis(2-ethylhexyl)thiophene (S1a). 3,4-Dibromothiophene (FUJIFILM Wako, 98% 17.8 g, 73.4 mmol) and Ni(dppp)Cl₂ (TCI, >98% 0.992 g, 1.84 mmol, 0.025 eq.) were added to a 1.0 L two-necked flask purged with an N₂ atmosphere. After dissolving them in anhydrous diethyl ether (Et₂O, FUJIFILM Wako, 400 mL), the solution was cooled down to 0 °C. A THF solution of 2-ethylhexylmagnesium bromide (1.0 M, 257.0 mmol, 3.5 eq.) was dropwisely added. The reaction mixture was then stirred at reflux temperature overnight, followed by quenching with sat. NH₄Cl aq. at 0 °C. The resultant solution was extracted with Et₂O and washed with water and brine. The organic phase was dried over anhydrous magnesium sulfate (MgSO₄), rotary-evaporated and purified by silica gel chromatography using hexane as an eluent to afford **S1a** (containing 24 mol% of mono-alkylated compounds (**S1a'**) which was removed in the next stage) as a colorless oil (23.0 g, quant.).

¹H NMR (400 MHz, CDCl₃): δ 7.21-7.17 (m, 1H), 6.88 (d, *J* = 6.8 Hz, 1H), 6.82 (s, 2H), 2.54 (d, *J* = 6.8 Hz, 0H), 2.50 (d, *J* = 7.2 Hz, 1H), 2.41 (d, *J* = 6.8 Hz, 4H), 1.54 (t, *J* = 5.9 Hz, 2H), 1.35-1.17 (m, 43H), 0.89-0.79 (m, 28H)

Synthesis of 3,4-bis(2-ethylhexyl)thiophene-2-calbaldehyde (S2a). S1a (19.8 g, 64.1 mmol) was placed in a 500 mL two-necked flask purged with N₂. After dissolving it in anhydrous THF (300 mL), *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine (TMEDA, >98%, TCI, 7.6 mL, 64.1 mmol, 1.0 eq.) was added and the solution was then cooled down to -78 °C. A 2.6 M hexane solution of *n*-BuLi (54 mL, 141 mmol, 2.2 eq.) was dropwisely added. The reaction mixture was stirred at

−78 °C for 30 min and at −30 °C for 2 h, respectively. Anhydrous *N*,*N*-dimethylformamide (DMF, FUJIFILM Wako, 39.8 mL, 513 mmol, 8.0 eq.) was dropwisely added to the solution at −30 °C. The reaction mixture was then warmed to −10 °C and stirred for 2 h, followed by quenching with sat. NH₄Cl aq. The resultant solution was extracted with ethyl acetate (EtOAc) and washed with water and brine. The organic phase was dried over anhydrous MgSO₄. The crude product was purified by silica gel chromatography using hexane/EtOAc (19/1) as an eluent to afford **S2a** as a yellow oil (9.46 g, 44%). ¹H NMR (400 MHz, CDCl₃): *δ* 9.99 (s, 1H), 7.31 (s, 1H), 2.81 (d, *J* = 7.7 Hz, 2H), 2.46 (d, *J* = 7.2 Hz, 2H), 1.57-1.49 (m, 2H), 1.43-1.18 (m, 22H), 0.94-0.81 (m, 15H). ¹³C NMR (101 MHz, CDCl₃): *δ* 182.9, 151.0, 143.8, 139.0, 130.9, 41.5, 39.6, 32.9, 32.5, 31.6, 28.9, 25.8, 23.0, 14.1, 11.0, 10.8. Anal.Calcd. for C₂₁H₃₆OS (%): C, 74.9; H, 10.8; S, 9.53; Found (%): C, 75.68; H, 11.46; S, 8.18.

Synthesis of 5-(bromomethyl)-3,4-bis(2-ethylhexyl)thiophene-2-calbaldehyde (S3a). S2b (8.56 g, 25.4 mmol) and hydrobromic acid (TCI, 47 wt% in water, 191 mL) were placed in a 300 mL three-necked flask with a condenser purged with N₂. After the mixture was cooled down to 0 °C, sulfuric acid (conc., Kanto, 62 mL), trioxane (TCI, >99% 4.5 g, 50.8 mmol, 2.0 eq.) and tetradecyltrimethylammonium bromide (TCI, >98%, 0.839 g, 2.54 mmol, 0.1 eq.) were added and stirred at 80 °C for 5 h. Then, the reaction mixture was poured into water (300 mL). The solution was extracted with chloroform, washed with water and brine. The organic phase was dried over by anhydrous MgSO₄, rotary-evaporated and purified by silica gel chromatography using hexane/EtOAc (9/1) as an eluent to afford S3b (containing 38 mol% of starting material (S2b) which was removed in the next stage) as a yellow oil (6.65 g). ¹H NMR (400 MHz, CDCl₃): δ 9.99 (s, 1H), 4.63 (s, 2H), 2.52 (d, *J* = 7.7 Hz, 2H), 1.54-1.47 (m, 2H), 1.36-1.20 (m, 22H), 0.92-0.85 (m, 12H).

Synthesis of diethyl ((3,4-bis(2-ethylhexyl)-5-formylthiophen-2-yl)methyl)phosphonate (1a).² S3a (8.46 g, 19.7 mmol), triethyl phosphite (TCI, >97%, 26 g, 158 mmol, 8.0 eq.), anhydrous dichloromethane (FUJIFILM Wako,100 mL) were placed in a 200 mL one-necked flask purged with N₂. The solution was cooled to 0 °C, and ZnBr (TCI, >98%, 7.09 g, 31.5 mmol, 1.6 eq.) was then added. The reaction mixture was warmed to room temperature and stirred 4 h, followed by quenching with sat. sodium hydrogen carbonate (NaHCO₃) aq.. The resultant solution was extracted with EtOAc and washed with water and brine. The organic phase was

dried over anhydrous MgSO₄. The crude product was purified by silica gel chromatography using hexane/EtOAc (6/4) as an eluent. The combined solution was stirred with activated carbon for 5 min to remove byproducts coloured in red, followed by filtering through a filter paper (ADVANTEC 5C). The filtrate was evaporated and dried in vacuo to afford **1a** as a viscous reddish yellow oil (2.5 g, 26%). ¹H NMR (400 MHz, CDCl₃): δ 9.95 (s, 1H), 4.10-4.03 (m, 4H), 3.34 (d, *J* = 22.2 Hz, 2H), 2.79 (d, *J* = 7.2 Hz, 2H), 2.51 (d, *J* = 7.7 Hz, 2H), 1.49-1.295 (m, 2H), 1.34-1.26 (m, 22H), 0.90-0.84 (m, 12H). ¹³C NMR (101 MHz, CDCl₃): δ 182.3, 151.6, 142.0, 141.9, 138.7, 138.6, 136.9, 62.6, 42.0, 40.5, 32.5, 31.9, 31.0, 28.9, 28.6, 27.2, 25.7, 23.0, 16.3, 14.0, 11.1. Anal.Calcd. for C₂₆H₄₇O₄PS (%): C, 64.17; H, 9.73; S, 6.59; Found (%): C, 61.78; H, 10.19; S, 6.15.

Synthesis of P3,4EHTV. Anhydrous THF (9 mL), 15-crown-5 (>98%, Aldrich, 0.1 mL, 1.05 eq.), a THF solution of sodium hexamethyldisilazide (NaHMDS, TCI, 1.9 M, 0.27 mL, 1.05 eq.) were placed in a 20 mL two-necked flask purged with N₂. The monomer **1a** (239 mg, 0.491 mmol, 1.00 eq.) solution in THF (1 mL) was also prepared in another 10 mL two-necked flask. After stirring for 10 min at room temperature, both of 20 mL and 10 mL two-necked flasks were cooled to -78 °C and stirred 10 min. Then, the monomer solution was added to the former 20 mL two-necked flask. After stirring for 5 min, a THF solution of hexanal (0.0426 M, 77 µL, 1/150 eq.) was added to start polymerization. The reaction mixture was warmed to -40 °C and stirred for 4 h. The polymerization mixture was quenched by 5M HCl and poured into methanol (MeOH)/H₂O (2:1, by vol) to precipitate the crude polymer. After filtering, it was purified by Soxhlet extraction with methanol, acetone, and recovered with hexane (24 h for each). After evaporating hexane, the polymer was freeze-dried from its benzene solution to afford P3,4EHTV as a dark blue solid (190 mg, 80%).



Figure S1. ¹H NMR spectrum of S1a measured in CDCl₃ (400 MHz).



Figure S2. ¹H NMR spectrum of S2a measured in CDCl₃ (400 MHz).



Figure S3. ¹³C NMR spectrum of S2a measured in CDCl₃ (101 MHz).



Figure S4. ¹H NMR spectrum of S3a measured in $CDCl_3$ (400 MHz).



Figure S5. ¹H NMR spectrum of **1a** measured in CDCl₃ (400 MHz).



Figure S6. ¹³C NMR spectrum of **1a** measured in CDCl₃ (101 MHz).



Figure S7. ¹H NMR spectrum of P3,4EHTV measured in CDCl₃ (400 MHz).



Figure S8. SEC UV trace of P3,4EHTV (THF at 40 °C, λ = 270 nm).



Figure S9. (a) TGA (N₂ flow: 200 mL min⁻¹, heating scan: 10 °C min⁻¹) and (b) DSC (N₂ flow: 20 mL min⁻¹, 1^{st} cooling and 2^{nd} heating scans: 10 °C min⁻¹) thermograms of P3,4EHTV.



Figure S10. The normalized UV–vis spectra of P3EHT (orange) and P3,4EHTV (blue). (dashed line: solution; solid line: thin film).



Figure S11. UV–vis–NIR spectra of (a) pristine and BCF-doped P3EHT solution, and (b) pristine and BCF-doped P3,4EHTV solution.



Figure S12. UPS spectra of (a) P3EHT and (b) P3,4EHTV at low kinetic energy region (SECO region, left) and low binding energy region (HOMO region, right).



Figure S13. PESA spectra of undoped and doped (a) P3EHT and (b) P3,4EHTV.



Figure S14. ¹⁹F NMR spectra of 30% BCF-doped P3EHT and 20% BCF-doped P3,4EHTV.



Figure S15. Raman spectra of undoped (a) P3EHT and (b) P3,4EHTV thin films. The carbon atoms in the thiophene rings adjacent to the sulfur atom and atoms bonded to another carbon atom denoted as C_{α} and C_{β} , respectively.



Figure S16. AFM height images of undoped and BCF-doped P3EHT films (scale bar = 500 nm).



Figure S17. AFM phase images of undoped and BCF-doped P3EHT films (scale bar = 500 nm).



Figure S18. AFM height images of undoped and BCF-doped P3,4EHTV films (scale bar = 500 nm).



Figure S19. AFM phase images of undoped and BCF-doped P3,4EHTV films (scale bar = 500 nm).



Figure S20. 2D GIWAXS patterns of undoped and BCF-doped P3EHT thin films.



Figure S21. 2D GIWAXS patterns of undoped and BCF-doped P3,4EHTV thin films.



Figure S22. 2D GIWAXS pattern of drop-cast BCF thin film.



Figure S23. Diiodomethane contact angle of BCF, undoped P3EHT, 30% BCF-doped P3EHT, undoped P3,4EHTV, and 20% BCF-doped P3,4EHTV thin films.



Figure S24. The thermoelectric properties of the 30% BCF-doped P3EHT and 20% BCF-doped P3,4EHTV thin films as a function of temperature: (a) the electrical conductivity, (b) the Seebeck coefficient, and (c) the power factor.



Figure S25. (a) The Arrhenius plot of the temperature-dependent electrical conductivity of the doped P3,4EHTV and P3EHT films. (b) The correlation between Seebeck coefficient and conductivity of doped P3,4EHTV and P3EHT films. The solid black lines correspond to the fitting of Chabinyc's empirical relationship of $S \sim \sigma^{-1/4}$.³ The dashed gray lines correspond to *PF* values.



Figure S26. (a) Photograph of P3,4EHTV and P3EHTV solutions in chloroform, each with a concentration of 10 mg mL⁻¹. (b) Thickness-normalized UV–vis–NIR absorption spectra of BCF-doped P3EHTV.



Figure S27. The thermoelectric properties of the BCF-doped P3EHTV thin films as a function of doping molar ratio: (a) the electrical conductivity, (b) the Seebeck coefficient, and (c) the power factor.

Entry	Doping molar ratio [%]	$\sigma_{\sf avg}$ [S cm ⁻¹]	S _{avg} [μV K ⁻¹]	PF_{max} [μ W m ⁻¹ K ⁻²]	PF_{avg} [μ W m ⁻¹ K ⁻²]
P3,4EHTV	10	$(4.8 \pm 2.1) \times 10^{-2}$	344.3 ± 21.6	8.4×10^{-1}	(5.5 ± 1.7) × 10 ⁻¹
	20	(3.1 ± 2.5) × 10 ^{−1}	195.1 ± 15.6	1.47	1.17 ± 0.23
	30	$(3.2 \pm 0.9) \times 10^{-1}$	147.3 ± 8.7	8.6 × 10 ⁻¹	$(5.8 \pm 1.7) \times 10^{-1}$
	40	$(1.2 \pm 0.8) \times 10^{-1}$	121.3 ± 9.8	4.4 × 10 ⁻¹	$(1.9 \pm 1.6) \times 10^{-1}$
	50	$(3.4 \pm 1.6) \times 10^{-2}$	96.4 ± 14.5	7.7 × 10 ⁻²	(3.5 ± 2.6) × 10 ⁻²
	80	(4.9 ± 3.3) × 10 ^{−3}	42.4 ± 11.9	7.6 × 10 ⁻⁴	(3.8 ± 3.5) × 10 ⁻⁴
РЗЕНТ	20	$(2.0 \pm 1.2) \times 10^{-2}$	179.6 ± 12.0	1.1×10^{-1}	$(6.2 \pm 3.2) \times 10^{-2}$
	30	$(4.1 \pm 2.2 \times 10^{-2})$	164.7 ± 14.6	1.7 × 10 ⁻¹	$(1.1 \pm 0.6) \times 10^{-1}$
	40	$(2.5 \pm 1.5) \times 10^{-2}$	158.0 ± 24.1	7.3 × 10 ⁻²	$(5.4 \pm 2.3) \times 10^{-2}$
	50	$(2.3 \pm 2.1) \times 10^{-2}$	163.6 ± 28.8	8.6 × 10 ⁻²	$(4.9 \pm 3.3) \times 10^{-2}$
	80	$(1.1 \pm 1.3) \times 10^{-2}$	174.1 ± 22.0	1.1 × 10 ⁻¹	$(4.7 \pm 3.8) \times 10^{-2}$
	100	$(1.0 \pm 1.1) \times 10^{-2}$	168.8 ± 22.6	5.1 × 10 ⁻²	(3.0 ± 2.0) × 10 ⁻²

Table S1. Summary of thermoelectric properties of BCF-doped P3EHT and P3,4EHTV thin films.

References

- 1 E. Goto, Y. Ochiai, M. Ueda and T. Higashihara, *Polym. Chem.*, 2018, **9**, 1996-2001.
- 2 G. G. Rajeshwaran, M. Nandakumar, R. Sureshbabu and A. K. Mohanakrishnan, *Org. Lett.*, 2011, **13**, 1270-1273.
- A. M. Glaudell, J. E. Cochran, S. N. Patel and M. L. Chabinyc, *Adv. Energy Mater.*, 2015, **5**, 1401072.