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Supplementary Information for

## The Effect of Aromatic Ring Size in Electron Deficient Semiconducting Polymers for n-type Organic Thermoelectrics

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#### 1. General procedures and experimental details:

All chemical reagents and starting materials were purchased from commercial sources and used without further purification. Reactions were carried out on a standard Schlenk line technique under a nitrogen atmosphere using solvents and reagents as commercially supplied.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with Bruker 500 MHz AVANACIII NMR spectrometer equipped with CryoProbe (BrukerBioSpin,Rheinstetten, Germany). Residual proton peaks are 7.26 ppm for CDCl<sub>3</sub> and 2.52\3.34 ppm for DMSO-d<sub>6</sub>. High-resolution Mass Spectra (HRMS) were recorded on a Bruker HRMS MICROTOF II spectrometer. Gas Chromatography-Mass Spectrometry (GC-MS) measurements were carried out on Angilent 7890B GC system with Agilent 5977A MSD, and Agilent 7693 auto sampler. The polymer molecular weights (numberaverage Mn and weight-average Mw) and polydispersity were measured using an Agilent Technologies PL-GPC 220 High Temperature gel permeation chromatography in 1,2,4trichlorobenezene (TCB) as the mobile phase at 150 °C. Absorption spectra were recorded on Varian Cary 5000 spectrophotometer by preparing polymer solutions in chlorobenzene and spincoated polymer films onto pre-treated glass substrates. Photo Electron Spectroscopy in Air (PESA) measurements were recorded with a Riken Keiki AC-2 PESA spectrometer with a power setting of 5nW and a power number of 0.3. Samples for PESA were prepared on glass substrates by spincoating. Thermal gravimetric analyses (TGA) were performed under a N<sub>2</sub> atmosphere using TA Instruments Trios V4.3.1.39215, at a heating rate of 10 °C min<sup>-1</sup>. Differential scanning calorimetry (DSC) analyses were performed on a METTLER TOLEDO Instrument DSC822 calorimeter with a heating rate of 10°C/min, two heating-cooling cycles from RT to- 300 °C under nitrogen atmosphere.

Density functional theory (DFT) calculations were performed on tetramers of the three polymers. In each case, the long solubilizing alkyl chains were replaced by shorter methyl groups in order to simplify the simulations. All calculations were performed employing the Gaussian-09 software. All geometries were optimized at the  $\omega$ B97XD/6-31G\*\* level of theory without any constraints.

2. Synthetic routes of the compounds:

The synthetic procedures for the preparation of (4-Bromobutyl)tricosane (R1), (4-Bromobutyl)nonadecane (R2)<sup>1</sup>, Bisisatin, N,N'-bis(5-decylheptadecyl), bisisatin (M1), N,N'-bis(5-octylpentadecyl)bisisatin(M2)<sup>2</sup>, benzo[1,2-b-4,5-b']difuran-2,6-(3H,7H)-dione (M3)<sup>3</sup> and naphtho-[1,2-b:5,6-b']difuran-2,7(3H, 8H)-dione (M4)<sup>4</sup> were inspired and modified from published literatures.

### 2.1 Synthesis of the Alkyl chains:

Synthesis of (4-Bromobutyl)tricosane (R1) :



Synthesis of (a): NBS (25g, 140 mmol) was added slowly in portions to a solution of 2-decyl-1tetradecanol (42g, 120 mmol) and triphenylphosphine (34g, 130 mmol) in DCM (250mL) at 0°C.The resulting mixture was stirred overnight to give a brown solution. The solvent was removed under vacuum. The solids were extracted with petroleum spirit (3 x 50 mL), to give a yellow oil which was purified by column chromatography (silica gel, petroleum spirit), to afford

as a colorless oil (44.5 g, 89% yield). 1H NMR (500 MHz, Chloroform-d) δ 3.47 (d, J = 4.8 Hz, 2H), 1.61 (h, J = 6.1 Hz, 1H), 1.47 – 1.10 (m, 41H), 0.91 (t, J = 6.6 Hz, 6H). 13C NMR (101 MHz, Chloroform-d) δ 39.60, 39.50, 32.56, 31.91, 29.78, 29.68, 29.67, 29.65, 29.63, 29.59, 29.36, 29.34, 26.55, 22.68, 14.09. GC-MS (m/z): 337.5 [M+–Br]

Synthesis of (b): 2-decyl-1-tetradecyl bromide (22 g, 53 mmol) was dissolved in anhydrous THF (110 mL), the resulting solution was bubbled with nitrogen for 30 min. Allylmagnesium bromide (40 mL of a 2.0 M solution in THF, 79 mmol) was added and the resulting solution heated at reflux for 48 hrs. The reaction was quenched with water (55 mL) and sulfuric acid (110 mL of 10 wt%) and extracted with Et2O (3 x 100 mL), washed with brine (3 x 100 mL), and dried over MgSO4. The solvent was removed under vacuum. The crude product was purified by column chromatography (silica gel, petroleum spirit), to afford a colorless oil (19 g, 93% yield). GC-MS (m/z): 378.4 [M+]

Synthesis of (c): 11-(but-3-enyl)tricosane (19 g, 50 mmol) was added to anhydrous diglyme (47 mL). to this solution NaBH4 (2 g, 60 mmol) was added and stirred at RT for 30 min. To the resulting mixture BF3.OEt2 (4.4 mL, 35 mmol) was added dropwise and stirred for 2 hrs. 3M NaOH (20mL) and water (5 mL) were added slowly and the mixture was stirred for another 2 hrs at 40°C. Followed by dropwise addition of H2O2 (20 mL). The resulting mixture was stirred at RT overnight and poured to water (60mL). The organic solvent was extracted with Et2O (3 x 40 mL), washed with saturated NaHCO3 (3 x 60 mL) and brine (3 x 60 mL), then dried over MgSO4. The solvent was removed under vacuum. The crude product was purified by column

chromatography (silica gel, petroleum spirit: Ethyl acetate (4:1)), to afford as a colorless oil (16.8 g, 85% yield). GC-MS (m/z): 395.5 [M+–H]

Synthesis of Alkyl1: NBS (16g, 40 mmol) was added slowly in portions to a solution of 5-decy-1-heptadecanol (10.5 g, 59.2 mmol) and TriphenylPhosphine (14 g, 54 mmol) in DCM (100mL) at 0°C. The resulting mixture was stirred overnight to give a brown solution. The solvent was removed under vacuum. The dark purple solids were extracted with petroleum spirit (3 x 80 mL), to give a yellow oil which was purified by column chromatography (silica gel, petroleum spirit), to afford as a colorless oil (16 g, 88% yield). 1H NMR (500 MHz, Chloroform-d)  $\delta$  3.43 (t, J = 6.9 Hz, 2H), 1.86 (p, J = 7.0 Hz, 2H), 1.46 – 1.38 (m, 3H), 1.27 (d, J = 18.7 Hz, 44H), 0.91 (t, J = 6.9 Hz, 6H). 13C NMR (126 MHz, Chloroform-d)  $\delta$  37.26, 33.98, 33.56, 33.30, 32.75, 31.98, 30.17, 29.76, 29.43, 26.68, 25.32, 22.75, 14.17. , GC-MS (m/z): 459.4 [M+]

Synthesis of (4-Bromobutyl)nonadecane (R2):



Synthesis of (a): NBS (25g, 140 mmol) was added slowly in portions to a solution 2-Octyl-1dodecanol (42g, 120 mmol) and TriphenylPhosphine (34g, 130 mmol) in DCM (250mL) at 0°C. The resulting mixture was stirred overnight to give a brown solution. The solvent was removed under vacuum. The solids were extracted with petroleum spirit (3 x 50 mL), to give a yellow oil which was purified by column chromatography (silica gel, petroleum spirit), to afford as a colorless oil (44.5 g, 89% yield). 1H NMR (500 MHz, , Chloroform-d)  $\delta$  3.45 (d, J = 4.8 Hz, 2H), 1.67 – 1.55 (m, 1H), 1.39 – 1.20 (m, 32H), 0.88 (t, J = 6.8 Hz, 6H). 13C NMR (125 MHz, Chloroform-d)  $\delta$  39.89, 39.65, 32.71, 32.07, 32.05, 29.94, 29.79, 29.78, 29.75, 29.71, 29.50, 29.46, 26.71, 22.85, 22.83, 14.27. GC-MS (m/z): 281.3 [M+–Br]

Synthesis of (b): 2-Octyl-1-dodecyl bromide (22 g, 53 mmol) was dissolved in anhydrous THF ( 110 mL), the resulting solution was bubbled with nitrogen for 30 min. Allylmagnesium bromide (40 mL of a 2.0 M solution in THF, 79 mmol) was added and the resulting solution heated at reflux for 48 hrs. The reaction was quenched with water (55 mL) and sulfuric acid (110 mL of 10 wt%) and extracted with Et2O (3 x 100 mL), washed with brine (3 x 100 mL), and dried over MgSO4. The solvent was removed under vacuum. The crude product was purified by column chromatography (silica gel, petroleum spirit), to afford as a colorless oil (19 g, 93% yield). GC-MS (m/z): 322.5 [M+]

Synthesis of (c): 9-(but-3-enyl) nonadecane (19 g, 50 mmol) was added to anhydrous diglyme (47 mL). to this solution NaBH4 (2 g, 60 mmol) was added and stirred at RT for 30 min. to the resulting mixture BF3.OEt2 (4.4 mL, 35 mmol) was added dropwise and stirred for 2 hrs. 3M NaOH (20mL) and water (5 mL) were added slowly and the mixture was stirred for another 2 hrs at 40°C.

Followed by dropwise addition of H2O2 (20 mL). The resulting mixture was stirred at RT overnight. The organic solvent was extracted with Et2O (3 x 100 mL), washed with saturated NaHCO3 (3 x 100 mL) and brine (3 x 100 mL), then dried over MgSO4. The solvent was removed under vacuum. The crude product was purified by column chromatography (silica gel, petroleum spirit: Ethyl acetate (4:1)), to afford as a colorless oil (19 g, 93% yield). GC-MS (m/z): 341.3 [M+–H]

Synthesis of Alkyl2: NBS (25g, 140 mmol) was added slowly in portions to a solution of 5-octyl-1pentadecanol (42g, 120 mmol) and TriphenylPhosphine (34g, 130 mmol) in DCM (250mL) at 0°C.The resulting mixture was stirred overnight to give a brown solution. The solvent was removed under vacuum. The solids were extracted with petroleum spirit (3 x 50 mL), to give a yellow oil which was purified by column chromatography (silica gel, petroleum spirit), to afford as a colorless oil (44.5 g, 89% yield). 1H NMR (500 MHz, Chloroform-d)  $\delta$  3.43 (t, J = 6.9 Hz, 2H), 1.86 (p, J = 7.0 Hz, 2H), 1.42 (p, J = 7.6 Hz, 2H), 1.37 – 1.15 (m, 36H), 0.91 (t, J = 6.9 Hz, 6H). 13C NMR (126 MHz, Chloroform-d)  $\delta$  37.26, 33.99, 33.30, 32.75, 31.97, 30.17, 29.76, 29.42, 26.68, 25.32, 22.74, 14.17. GC-MS (m/z): 322.4 [M+–Br]

#### 2.2 Monomer Synthesis

Synthesis of N-alkylated bisisatin core monomers (Monomer1 & 2):



Synthesis of Bisisatin (1) :

1,5-Diaminonaphthalene (4 g, 25 mmol) was dissolved in (41 mL) glacial acetic acid and heated to reflux. To the resulting dark purple solution was added dropwise, diethylketomalonate (32 mL, 205 mmol) in glacial acetic acid (46 mL). The resulting mixture was heated to 150°C overnight. The solvent was removed under vacuum and 1M NaOH was added to the resulting dark brick red solids until complete dissolution to a final pH of (11-12). The resulting mixture was poured brown solution was heated at 150°C overnight with sparging air into the solution. The resulting mixture was poured onto ice and 6M HCl was added until pH=0 to give a purple precipitate, which was filtered and washed with water to give dark red-purple solids (6 g, 93% yield) and carried out without further purification. ). 1H NMR (500 MHz, DMSO-d6)  $\delta$  11.77 (s, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H). 13C NMR (126 MHz, DMSO-d6)  $\delta$  183.85, 152.36, 124.50, 120.51, 117.60, 115.75.

Synthesis of N,N'-bis(5-decylheptadecyl)bisisatin (M1):

To a mixture of crude () (g,mmol) and dry K2CO3 (g) in anhydrous DMF (mL), was added 5-decy-1-heptadecyl bromide (g,mmol). The resulting mixture was stirred at 70°C for 4 hours. The reaction mixture was poured over H2O and acidified with 1M HCl to pH of 7. The aqueous layer was extracted with DCM, washed with H2O, brine and dried over MgSO4. The solvent was removed under vacuum. The crude Viscous dark purple oil was purified by column chromatography (silica gel, DCM:petroleum spirit (7:3)), followed by precipitation in MeOH and filtered to afford the product as dark blue solids (1 g, 11% yield). 1H NMR (500 MHz, Chloroformd)  $\delta$  7.97 (d, J = 8.7 Hz, 1H), 7.70 (d, J = 8.7 Hz, 1H), 4.25 (t, J = 7.6 Hz, 2H), 1.82 (p, J = 7.7 Hz, 2H), 1.59 (s, 3H), 1.49 – 1.39 (m, 2H), 1.36 – 1.10 (m, 48H), 0.90 (t, J = 6.8 Hz, 7H). 13C NMR (126 MHz, Chloroform-d)  $\delta$  182.81, 158.99, 152.21, 127.28, 119.63, 116.19, 43.56, 37.30, 33.29, 31.95, 30.15, 29.74, 29.40, 26.66, 23.93, 22.72, 14.17. HRMS (m/z): (M·+) calc. (C68H114N2O4): 1022.87786. found: 1023.88593.

### Synthesis of N,N'-bis(5-octylpentadecyl)bisisatin (M2):

To a mixture of crude () (3 g, 11 mmol) and dry K2CO3 (8 g) in anhydrous DMF (65 mL), was added 5-decy-1-heptadecyl bromide (20 g, 49.5mmol). The resulting mixture was stirred at 70°C for 4 hours. The reaction mixture was poured over H2O and acidified with 1M HCl to pH of 7. The aqueous layer was extracted with DCM, washed with H2O, brine and dried over MgSO4. The solvent was removed under vacuum. The crude Viscous dark purple oil was purified by column chromatography (silica gel, DCM: Petroleum spirit (7:3)), followed by precipitation in MeOH and filtered to afford the product as dark blue solids (2.5 g, 25% yield). 1H NMR (500 MHz, Chloroform-d)  $\delta$  7.97 (d, J = 8.7 Hz, 1H), 7.70 (d, J = 8.6 Hz, 1H), 4.30 – 4.19 (m, 2H), 1.82 (p, J = 7.8 Hz, 2H), 1.59 (s, 4H), 1.49 – 1.39 (m, 2H), 1.37 – 1.06 (m, 39H), 0.90 (t, J = 6.6 Hz, 6H).

13C NMR (126 MHz, Chloroform-d) δ 182.81, 158.99, 152.21, 127.28, 120.27, 119.63, 116.20, 43.56, 37.29, 33.48, 33.29, 31.94, 30.15, 29.79, 29.74, 29.70, 29.68, 29.39, 26.66, 23.93, 22.72, 14.17. HRMS (m/z): (M·+) calc. (C68H114N2O4): 910.75266. found: 911.75935.

Synthesis of benzo[1,2-b-4,5-b']difuran-2,6-(3H,7H)-dione (M3):



Synthesis of (2):

To a three-neck round-bottom flask equipped with two dropping funnels was added ethyl cyanoacetate (4.21 g, 4 ml, 37.25 mmol) in ethanol (15 ml). to the solution, concentrated ammonium hydroxide (3.17 g, 3.5 ml, 90.62 mmol) was added.in one dropping funnel was added ammonium hydroxide (11.28 g, 12.5 ml, 322 mmol) in water (20 ml) was added. Meanwhile, to a solution of ethyl cyanoacetate (6.4 g, 6 ml, 56 mmol) in ethanol (50 ml) was added p-benzoquinone (5 g, 46 mmol), the resulting solution was stirred at 40 °C for 30 min and transferred while hot to the other dropping funnel. The solutions in both dropping funnels were delivered to the flask at the same time with uniform rate. all the ammonium hydroxide solution should be added by the time 90% of the p-benzoquinone solution has been added. After completion of the addition, the resulting solution was stirred at RT for 1 hour. The precipitates formed were filtered under vacuum and washed with ethanol and dried to get Compound 2 (3.01g, 20%yield) as ashy purple solid.

Synthesis of (3):

To a residue of 1 (3 g, 9 mmol) was added concentrated HCl (0.027 g, 23 ml, 0.76 mmol) and water (18 mL) and the resulting solution was refluxed at 110°C overnight. Water (15 ml) and celite (1.5 g) were added to the hot reaction mixture and stirred for 5 min, after which it is rapidly filtered with suction and the filtrate was taken and cooled. White creamy crystals have been collected upon filtration 3 (1.42g, 59% yield).

Synthesis of (M3):

To a residue of 2 (1.4g, 6.2 mmol) in anhydrous toluene (75 mL), acetic anhydride (16.4 g, 15 ml, 195.96 mmol). The resulting mixture was stirred at 100°C overnight. The solvent was removed under vacuum, to the resulting solids was added chloroform and filtered, the filtrate was recrystallized in toluene to give the pure final product as beige crystals (0.1g, 26% yield). 1H NMR (500 MHz, DMSO-d6)  $\delta$  7.25 (s, 1H), 3.96 (s, 2H). 13C NMR (126 MHz, DMSO-d6)  $\delta$  174.85, 150.57, 124.42, 107.81, 33.78. HRMS (m/z): (M·+) calc. (C68H114N2O4): 910.75266. found: 911.75935.

Synthesis of naphtho-[1,2-b:5,6-b']difuran-2,7(3H, 8H)-dione (M4):



Synthesis of (4):

1,5-dihydroxynaphtelene (4.2 g, 26 mmol) was dissolved in DMSO (105 ml), to which grinded pellets of NaOH was added (2.3 g, 56.9 mmol) and the resulting mixture was stirred at RT for 2 h, then 1,1,2-trichloroethylene (7 ml, 78 mmol) was slowly added. The resulting mixture was stirred at RT overnight. Water was slowly added (100 mL). The two phases were separated and the aqueous layer was extracted with DCM, washed with brine and dried over MgSO4 and the solvent was removed under vacuum. The crude product was purified by column chromatography (silica gel, petroleum spirit)), to afford 4 as a colorless solid (3 g, 33% yield). 1H NMR (500 MHz, Chloroform-d)  $\delta$  8.07 (d, J = 8.5 Hz, 1H), 7.53 (t, J = 8.1 Hz, 1H), 7.16 (d, J = 7.6 Hz, 1H), 6.10 (d, J = 1.2 Hz, 1H), 13C-NMR (75 MHz, Chloroform-d)  $\delta$  149.94, 140.53, 127.32, 126.40, 119.01, 111.98, 105.32.

Synthesis of (5):

Compound 4 (3 g, 8.57 mmol) was dissolved in Et2O (60 ml). the mixture was cooled to -78°C to which 2.5 M solution of n-BuLi in hexane (28 mL, 68.5 mmol) was slowly added and stirred at - 78°C for 1 hour and subsequently warmed to -40°C and stirred for 2 hours at the same temperature. Water was slowly added (60 mL). The two phases were separated and the aqueous layer was extracted with hexane, , washed with saturated NH4Cl, then brine and dried over MgSO4 and the solvent was removed under vacuum to afford 5 as pale brown solids which was directly used for the next step without further purification due to its instability

Synthesis of (M4):

In 1,4 dioxane (22 mL), was added tetrafluoroboric acid diethyl ether complex (0.23 ml, 1.7 mmol) and 2,6-Dimethylpyridine N-oxide (2 ml, 17 mmol). Afterwards, Compound 5 (1.78g, 8.5 mmol) was added and the resulting mixture was stirred at 80°C overnight. The solvent was removed under vacuum, then methanol was added to form a precipitate, which was collected by filtration. The solids were dissolved in hot toluene the undissolved solids were filtered off. The filtrate was taken and the solvent was removed under vacuum. The resulting solids were dissolved in acetone, the undissolved solids were collected by filtration to afford the final pure product as pale brown solids (10 mg, 5% Yield). 1H NMR (500 MHz, DMSO-d6)  $\delta$  7.75 (d, J = 8.3 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 4.15 (s, 2H). 13C NMR (126 MHz, DMSO-d6)  $\delta$  174.95, 149.98, 123.65, 120.29, 119.41, 116.39, 34.27. HRMS (m/z): (M·+) calc. (C68H114N2O4): 910.75266. found: 911.75935.

2.3 Polymer Synthesis:

The synthetic procedure for the polymers were tailored from literature<sup>5</sup>.

Synthesis of P1:



A microwave vial was charged with N,N'-bis(5-decylheptadecyl)bisisatin (109 mg, 0.106 mmol), benzo[1,2-b-4,5-b']difuran-2,6-(3H,7H)-dione (20.27 mg, 0.106 mmol), p-toluene sulfonic acid monohydrate (6 mg, 0.0315 mmol ). Anhydrous toluene (1.5 mL) was injected. The resulting solution was purged with N2 for 30 min and the reaction was heated to 130°C for 4 hours. The reaction mixture changed color from dark purple to dark blue over the polymerization period. The crude polymer was precipitated in methanol and purified by Soxhlet extraction with methanol, acetone, hexane and finally chloroform. The chloroform fraction was collected and the solvent was removed under vacuum. Afterwards, the polymer precipitated into methanol, filtered and dried. Yield: 110 mg, 86 % dark blue solid. GPC (1,2,4-trichlorobenzene, 150 °C): Mn 14kDa, Mw

29kDa. <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.72-8.89 ppm (d), 3.55 ppm (t), 1.92 ppm (t), 0.67-1.75 ppm (broad).

Synthesis of P2:



A microwave vial was charged with N,N'-bis(5-octylpentadecyl)bisisatin (115 mg, 0.126 mmol), benzo[1,2-b-4,5-b']difuran-2,6-(3H,7H)-dione (23.99 mg, 0.126 mmol), p-toluene sulfonic acid monohydrate (6 mg, 0.0315 mmol ). Anhydrous toluene (1.5 mL) was injected. The resulting solution was purged with N2 for 30 min and the reaction was heated to 130°C for 24 hours. The reaction mixture changed color from dark purple to dark blue over the polymerization period. The crude polymer was precipitated in methanol and purified by Soxhlet extraction with methanol, acetone, hexane and finally chloroform. The chloroform fraction was collected and the solvent was removed under vacuum. Afterwards, the polymer precipitated into methanol, filtered and dried. Yield: 59 mg, 43 % dark blue solid. GPC (1,2,4-trichlorobenzene, 80 °C): Mn 16kDa, Mw 27kDa.<sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  3.63 ppm (t), 1.89 ppm (t), 0.72-1.82 ppm (broad).

Synthesis of P3:



A microwave vial was charged with N,N'-bis(5-decylheptadecyl)bisisatin (85.23 mg, 0.083 mmol), naphtho-[1,2-b:5,6-b']difuran-2,7(3H, 8H)-dione (19.99 mg, 0.083 mmol), p-toluene sulfonic acid monohydrate (6 mg, 0.0315 mmol). Anhydrous toluene (1.5 mL) was injected. The resulting solution was purged with N2 for 30 min and the reaction was heated to 130°C for 8 hours. The reaction mixture changed color from dark purple to dark green over the polymerization period. The crude polymer was precipitated in methanol and purified by Soxhlet extraction with methanol, acetone, hexane and finally chloroform. The chloroform fraction was collected and the solvent was removed under vacuum. Afterwards, the polymer precipitated into methanol, filtered and dried. Yield: 46.85 mg, 45 % dark green solid. GPC (1,2,4-trichlorobenzene, 80 °C): Mn 14kDa, Mw 20kDa. <sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  7.73-7.90 ppm (d), 3.55 ppm (t), 1.92 ppm (t), 0.67-1.75 ppm (broad).





Figure 1. <sup>1</sup>H NMR spectrum of compound 1



Figure 2. <sup>13</sup>C NMR spectrum of compound 1







Figure 4. <sup>13</sup>C NMR spectrum of compound M1



Figure 6. <sup>13</sup>C NMR spectrum of compound M2



Figure 8. <sup>13</sup>C NMR spectrum of compound M3



Figure 10. <sup>13</sup>C NMR spectrum of compound M4



Figure 12. 1H NMR spectrum of polymer P2







## 4. UV-Vis absorbance spectroscopy

Figure 14. Thin films and solution UV-VIS absorbance of pristine and doped polymers

## 5. Gel permeation chromatography (GPC) measurements





6. Thermal gravimetric analysis (TGA)

Figure 15. TGA curves of a) P1, b) P2 and c) P3



7. Differential scanning calorimeter (DSC)

Figure 16. DSC measurements of a) P1, b) P2 and c) P3



### 8. Organic field effect transistor (OFET) measurements

Figure 17. Transistor properties of the polymers.

Photolithographyically defined interdigitated gold electrodes are used in this work, the thickness of which is 20 nm, and with a channel length of 20 um and a channel width of 1 mm, respectively. 30 nm semiconductor layer is spin-coated on top of cleaned electrodes, which is annealed at 200 degrees for half an hour to achieve optimal microstructure. After the annealing process, 500 nm PMMA layer is spin-coated on top of the semiconductor layer and annealed at 90 degrees for 20

minutes. Then for the final step, 30 nm aluminum is evaporated around the channel region on top of the PMMA layer to form the gate electrode and encapsulate the devices.

### 9. Thermoelectric measurements

All films were deposited inside a nitrogen-filled glovebox. Glass substrates were cleansed in water, acetone and isopropanol. P1, P2, and P3 solutions (all at 5 mg/ml) were obtained by dissolving the polymers in o-dichlorobenzene, and stirring at 100 °C for at least 10 h to ensure dissolution. The pristine films were obtained by spin-coating the warm solutions (70 °C) onto the substrates at 1000 rpm for 30 s. Afterwards, the films were thermally annealed at 110 °C on a hot template for 30 min, followed by cooling down to room temperature. For solution doping, polymer solutions in odichlorobenzene (5 mg/mL) and corresponding N-DMBI solution in o-dichlorobenzene (same molar concentration as the corresponding polymer) were firstly mixed in volume ratios, stirring at 70 °C for at least 1h. Then, the aforementioned warm solutions were spin-casted onto the glass substrates (1000 rpm, 30 s). Afterwards, the films were heated at 110 °C for 30 min and cooled down to ambient temperature. Electrical conductivity and Seebeck were both measured inside the nitrogen-filled glovebox using a Keithley 4200-SCS. For all measurements, prior to polymer layers deposition, 25 nm Au electrodes with a 5 nm Ti adhesion layer were firstly deposited on top of glass substrates. The electrodes dimensions for conductivity and Seebeck measurements were L/W = 30  $\mu$ m/1000  $\mu$ m and L/W = 0.5 mm/15 mm, respectively. Two Peltier elements were used to achieve a temperature gradient ( $\Delta T$ ) across the samples, and the thermovoltage ( $\Delta V$ ) was tested between two electrodes. The Seebeck was determined from the slope of  $\Delta V$  measured at six different AT values

10.2D-Grazing Incidence Wide Angle X-ray Scattering (GIWAXS)

2-D GIWAXS was carried out at the Advanced Photon Source at Argonne National Laboratory on beam line 8-ID-E at room temperature under vacuum with 10.92 keV ( $\lambda = 1.135$  Å) synchrotron radiation with a 0.14° incident angle and measured with a Pilatus 1M hybrid pixel array detector during 10 second exposures. GIWAXS samples were spin coated on Si wafer (University Wafer) substrates (~20 mm x 20 mm) from chloroform solutions (5 mg polymer/ml chloroform). Data analysis was carried out with GIXSGUI Matlab toolbox<sup>6</sup>.

		P1	P2	Р3
In-plane (100)	q (Å <sup>-1</sup> )	0.201	0.205	0.202
	d (Å)	31.3	30.7	31.1
In-plane $(010)$	q (Å-1)	1.740	1.733	1.746
	d (Å)	3.61	3.63	3.60
Out-of-plane (010)	q (Å <sup>-1</sup> )	1.736	1.722	1.741
	d (Å)	3.62	3.65	3.61

Table S1.GIWAXS scattering peak centers and d-spacing.

11. Density functional theory (DFT)



Figure 18. DFT-optimized geometries and molecular frontier orbitals of the trimmer of (a) and (b) P1 and P2, (c) and (d) P3.

### 12.References

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