SUPPORTING INFORMATION

REDUCING NON-RADIATIVE VOLTAGE LOSSES IN ORGANIC SOLAR CELLS USING MOLECULAR ENCAPSULATION

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1. General Synthesis

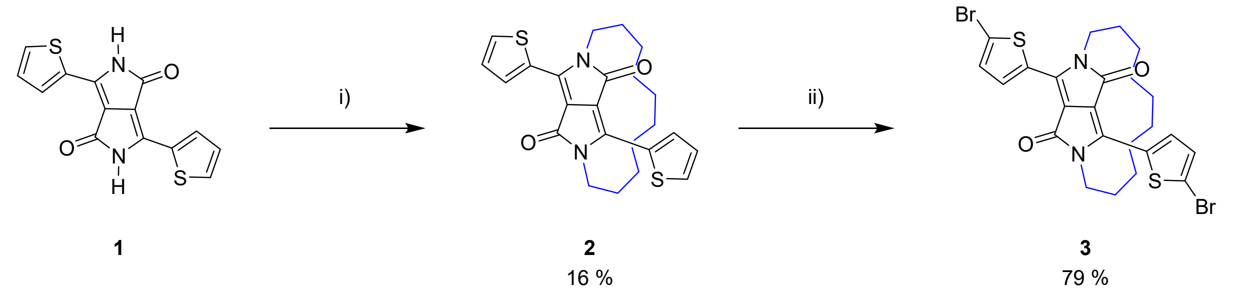
All moisture and air sensitive reactions were carried out in oven dried flasks under an inert argon atmosphere. R.T refers to 25˚C maintained by the use of a heating mantle. All reactions were covered with foil unless otherwise stated and were magnetically stirred. Merck Geduran® Si 60 silica gel or Biotage® Isolera™ Four with either Biotage® SNAP/ SNAP Ultra cartridges (10 g, 20 g, 50 g or 100 g) were used for column chromatography during purification. DC Fertigfolien ALUGRAM aluminium sheets coated with silica gel, were used for carrying out analytical thin layer chromatography (TLC). Compounds were visualised by ultra-violet light. Chemicals were used as supplied. Anhydrous solvents were supplied commercially and used under an inert argon atmosphere. All other solvents and reagents used were supplied commercially and used as received. 3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (Compound **1**), 2,5-bis(2-decyltetradecyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**DT-Alkylated DPP**), 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (Compound **4**), 2,5-bis(2-hexyldecyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**HD-Alkylated DPP**) and 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-hexyldecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (Compound **5**) were prepared according to previously reported procedures in literature.[1-3] Reference polymers **PDPP-TTref** and **PDPP-Pref** were synthesized according to previous literature.[4, 5]

2. Instrumental Techniques

^{1}H NMR were carried out at 400 MHz on an Avance III 400 HD Spectrometer or at 600 MHz on an Avance 600 BBI Spectrometer at the Department of Chemistry, University of Cambridge. The internal standard used was $CHCl_3$ (δ = 7.26 ppm s) and DMSO (δ = 2.50 ppm, s). ^{1}H NMR shifts were reported to the nearest 0.01 ppm and the following abbreviations were used: s, singlet; d, doublet; t, triplet; q, quartet; qn, quintet; sxt, sextet; m, multiplet; br, broad; Ar, aromatic; Th, thienyl; Ph, phenyl. The coupling constants(J) are measured in Hertz. ^{13}C NMR spectra were recorded at 125 MHz on a BRUKER DCH Cryoprobe Spectrometer in the stated solvent. The internal standard used was ^{13}C NMR $CHCl_3$ (δ = 77.2 ppm, t) and $(CD_3)_2SO$ (δ = 39.52 ppm, s). ^{13}C NMR chemical shifts are reported to the nearest 0.1 ppm. Mass spectra were obtained using a Waters LCT, Finnigan MAT 900XP or Waters MALDI micro MX spectrometer at the Department of Chemistry, University of Cambridge. UV-vis spectra were recorded on a Shimadzu UV-1800 spectrophotometer using Hellma® absorption cuvettes in chlorobenzene (~5 µg/mL), 200-2500 nm spectral range, pathlength 10 mm, chamber volume 3500 µL. GPC/SEC samples for the TT series were run at 80 °C at 2 mL/min on a Shimadzu Prominence instrument equipped with a differential refractive index and a UV-Vis detector. The mobile phase was chlorobenzene, and polystyrene was used as a standard for calibration. The analyte samples were filtered through a PTFE frit with 0.45 µm pore size before injection. The experimental molar mass (Mn, Mw,) and PDI values of synthesised polymers were obtained by using Shimadzu GPC/SEC software. GPC/SEC samples for the P series were run by Dr. Samuel Lawton, University of Warwick at 160 °C at 1 mL/min on a Agilent PL220 instrument equipped with differential refractive index (DRI) and viscometry (VS) detectors. The system was equipped with 2 x PLgel Olexis columns (300 x 7.5 mm) and an Olexis 10 µm guard column. The mobile phase was 1,2,4-trichlorobenzene, and polystyrene was used as a standard for calibration. The analyte samples were filtered through a 10 µm stainless steel frit prior to injection.

3. Synthesis and Characterization of Compounds

Synthesis of encapsulated DPP monomer 3



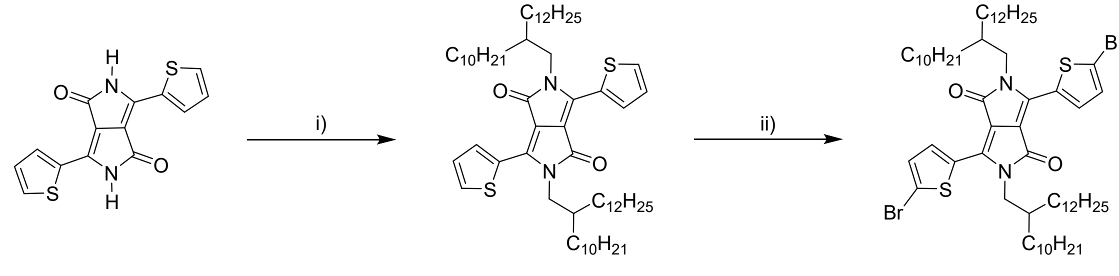
Synthesis of 2

To an oven dried 3-necked flask, equipped with a dropping funnel and under argon, was added K_2CO_3 (0.58 g, 1.66 mmol), 18-crown-6 (6.0 mg, 0.022 mmol), and anhydrous DMF (800 mL). The reaction mixture was then stirred and heated to 120 °C. To a second oven dried flask under argon, was added DPP (**1**) (0.5 g, 1.66 mmol), 1,10-dibromodecane (0.54 g, 1.66 mmol) and DMF (626 mL) which was degassed for 30 min, before dropwise addition into the reaction flask. The reaction mixture was then allowed to stir overnight at 120 °C, before cooling to RT. The solvent was then removed *in vacuo* and the crude product was purified *via* column chromatography (hexane: chloroform= 2:1), sonicated in hexane and collected *via* filtration to give the title compound as a bright pink solid (0.12 g, 0.27 mmol, 16%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.84 (dd, *J* = 3.9, 1.1 Hz, 2H, ThH), 7.63 (dd, *J* = 5.0, 1.1 Hz, 2H, ThH), 7.28 – 7.25 (m, 2H, ThH), 4.53 (ddd, *J* = 15.0, 10.8, 4.2 Hz, 2H, Alkyl Chain), 4.04 (dt, *J* = 15.0, 4.2 Hz, 2H, Alkyl Chain), 1.85 – 1.74 (m, 2H, Alkyl Chain), 1.65 – 1.52 (m, 2H, Alkyl Chain), 1.36 – 0.77 (m, 12H, Alkyl Chain).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.8, 141.1, 134.9, 130.7, 130.5, 128.5, 109.9, 42.8, 29.4, 28.9, 27.9, 26.0. **HRMS** (TOF MS ASAP+): Calculated for $C_{24}H_{26}N_2O_2S_2^+$: 439.1514. Found *m/z* 439.1502 $[M+H]^+$.

Synthesis of 3

To a 3-necked flask under argon was added **2** (0.11 g, 0.25 mmol) dissolved in chloroform (25 mL) and the reaction was cooled to 0 °C (30 min). N-bromosuccinimide (0.98 g, 0.55 mmol) was then added to the stirring solution and the reaction was covered from light. After cooling, the reaction was heated to 50 °C and was left to stir for 5 h. The resulting solution was then diluted with chloroform and concentrated *in vacuo*. Methanol was then added to the flask and the resulting suspension was then sonicated. The product was purified *via* column chromatography (chloroform), sonicated in methanol and collected by filtration to afford the pure dark purple solid product (0.12 g, 0.20 mmol, 79%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.60 (d, *J* = 4.2 Hz, 2H, ThH), 7.23 (d, *J* = 4.2 Hz, 2H, ThH), 4.51 (ddd, *J* = 15.2, 11.0, 4.1 Hz, 2H, Alkyl Chain), 3.89 (dt, *J* = 15.2, 4.1 Hz, 2H, Alkyl Chain), 1.87 – 1.75 (m, 2H, Alkyl Chain), 1.66 – 1.50 (m, 2H, Alkyl Chain), 1.34 – 1.06 (m, 6H, Alkyl Chain), 1.02 – 0.76 (m, 6H, Alkyl Chain).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.5, 140.0, 135.0, 131.9, 131.6, 119.3, 110.0, 42.9, 29.4, 28.9, 27.9, 25.9. **HRMS** (TOF MS ASAP+): Calculated for $C_{24}H_{25}Br_2N_2O_2S_2^+$: 594.9724. Found *m/z* 594.9714 $[M+H]^+$.

Synthesis of 4



1

DT-Alkylated DPP
23 %

4
79 %

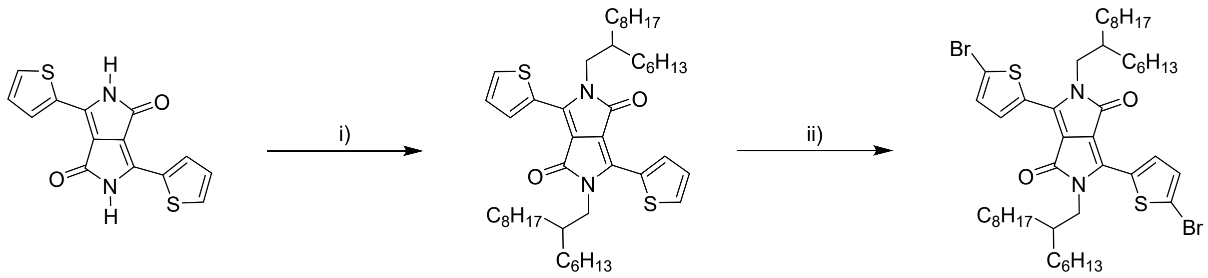
Synthesis of DT-Alkylated DPP

To an oven dried flask under argon was added DPP (**1)** (3.79 g, 12.6 mmol), K_2CO_3 (5.80 g, 42.0 mmol), 18-crown-6 (0.05 g, 0.19 mmol) and 7-(bromomethyl)pentadecane (12.8 g, 42.0 mmol), followed by anhydrous DMF (152 mL). The solution was then heated to 120 °C and was stirred for 18 h. The reaction mixture was then cooled to RT. Chloroform was then added to the flask and the solution was concentrated *in vacuo*. The crude product was then purified *via* column chromatography on silica gel (hexane: chloroform= 2:1) followed by recrystallisation in isopropanol to afford the product as a magenta solid (2.17 g, 2.9 mmol, 23%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.87 (dd, *J* = 3.9, 1.0 Hz, 2H, ThH), 7.62 (dd, *J* = 5.0, 1.0 Hz, 2H, ThH), 7.28 – 7.22 (m, 2H, ThH), 4.01 (d, *J* = 7.7 Hz, 4H, NCH_2), 1.90 (m, 2H, Alkyl Chain), 1.35 – 1.14 (m, 80H, Alkyl Chain), 0.87 (td, *J* = 6.8, 2.2 Hz, 12H, Alkyl Chain).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.8, 140.4, 135.2, 130.4, 129.8, 128.4, 107.9, 46.2, 37.8, 31.9, 31.2, 30.0, 29.7, 29.7, 29.6, 29.4, 29.4, 26.2, 22.7, 14.1. **HRMS** (TOF MS ASAP+): Calculated for $C_{62}H_{105}N_2O_2S_2^+$: 973.7617. Found *m/z* 973.7609 $[M+H]^+$.

Synthesis of 4

To a 3-necked flask under argon was added 2,5-bis(2-decyltetradecyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**DT-Alkylated DPP**) (1.20 g, 1.23 mmol) dissolved in chloroform (117 mL) and the reaction was cooled to 0 °C (30 min). *N*-bromosuccinimide (0.48 g, 2.71 mmol) was then added to the stirring solution and the reaction was covered from light. The reaction was then allowed to warm to RT and left to stir overnight. The resulting solution was then diluted with chloroform and concentrated *in vacuo*. The crude product was purified *via* column chromatography (hexane: chloroform= 1:2) followed by recrystallisation in isopropanol. The solid was then collected *via* filtration to give the title compound as a dark purple waxy solid (1.10 g, 0.97 mmol, 79%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.62 (d, *J* = 4.2 Hz, 2H, ThH), 7.22 (d, *J* = 4.2 Hz, 2H, ThH), 3.92 (d, *J* = 7.7 Hz, 4H, NCH_2), 1.87 (br s, 2H, NCH_2CH), 1.33 – 1.16 (m, 80H, Alkyl Chain), 0.87 (t, *J* = 6.8, 12H, CH_3).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.4, 139.4, 135.3, 131.4, 131.2, 119.0, 108.0, 46.4, 37.8, 31.9, 31.2, 30.0, 29.7, 29.6, 29.4, 26.2, 22.7, 14.1. **HRMS** (TOF MS ASAP+): Calculated for $C_{62}H_{103}Br_2N_2O_2S_2^+$: 1129.5828. Found *m/z* 1129.5780 $[M+H]^+$.

Synthesis of 5



1

HD-Alkylated DPP

26 %

5

68 %

Synthesis of HD-Alkylated DPP

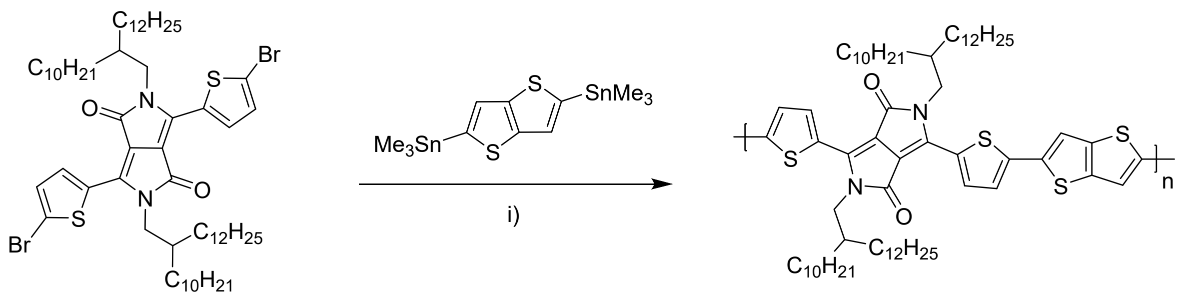
To an oven dried flask under argon was added compound **1** (3.79 g, 12.6 mmol), K_2CO_3 (5.80 g, 42.0 mmol), 18-crown-6 (0.05 g, 0.19 mmol), 7-(bromomethyl)pentadecane (12.8 g, 42.0 mmol), followed by anhydrous DMF (152 mL). The solution was then heated to 120 °C and was stirred for 18 h. The reaction mixture was then cooled to RT. Chloroform was then added to the flask and the solution was concentrated *in vacuo*. The crude product was then purified *via* column chromatography on silica gel (hexane: chloroform= 2:1) followed by recrystallisation in ethanol, to afford the product as a magenta solid (2.45 g, 3.27 mmol, 26%).^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.86 (dd, *J* = 3.9, 1.0 Hz, 2H, ThH), 7.62 (dd, *J* = 5.0, 1.0 Hz, 2H, ThH), 7.32 – 7.13 (m, 2H, ThH), 4.02 (d, *J* = 7.7 Hz, 4H, NCH_2), 1.90 (m, 2H, NCH_2CH), 1.35 – 1.04 (m, 48H, Alkyl Chain), 0.87-0.82 (m, 12H, Alkyl Chain). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 161.8, 140.4, 135.2, 130.5, 129.8, 128.4, 107.9, 46.2, 37.7, 31.9, 31.8, 31.2, 30.0, 29.7, 29.5, 29.3, 26.2, 26.1, 22.7, 22.6, 14.1. **LRMS** (EI+) *m/z* 748 $[M-H]^+$.

Synthesis of 5

To a flask under argon was added 2,5-bis(2-hexyldecyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**HD-Alkylated DPP**) (0.65 g, 0.87 mmol) dissolved in chloroform (82 mL) and the reaction was cooled to 0 °C (30 min). N-bromosuccinimide (0.39 g, 2.19 mmol) was then added to the stirring solution and the reaction was covered with foil. The reaction was then stirred for a further 30 min at 0 °C before allowing to warm to RT and was left to stir for 12 h. The resulting solution was then diluted with chloroform and concentrated *in vacuo*. Methanol was then added to the flask and the resulting suspension was sonicated and collected *via* filtration. The crude product was then purified *via* column chromatography on silica gel (chloroform), sonicated in methanol and collected by filtration to afford the product as a purple solid (0.54 g, 0.60 mmol, 68%).^{1}**H NMR** (600 MHz, $CDCl_3$) δ (ppm): 8.62 (d, *J* = 4.2 Hz, 2H, ThH), 7.22 (d, *J* = 4.2 Hz, 2H, ThH), 3.92 (d, *J* = 7.8 Hz, 4H, NCH_2), 1.95 – 1.75 (m, 2H, NCH_2CH), 1.37 – 1.11 (m, 48H, Alkyl Chain), 0.85 (m,12H, Alkyl Chain). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 161.5, 139.5, 135.5, 131.6, 131.3, 119.1, 108.1, 46.4, 37.9, 32.0, 31.9, 31.2, 30.1, 29.8, 29.6, 29.4, 26.3, 26.2, 22.8, 14.3, 14.2. **LRMS** (ESI+) *m/z* 905 $[M+H]^+$.

Synthesis of the DPP polymers – TT Series

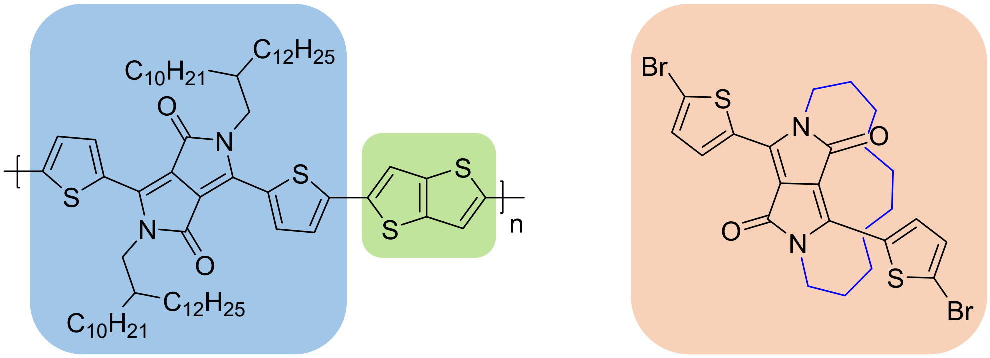
Reference Polymer PDPP-TTref



4

PDPP-TTref
77 %

Table S1. A summary of the monomer ratios, extraction solvents used to isolate the DPP polymers, yields, molecular weights, PDI and optical properties of the polymers in the study.

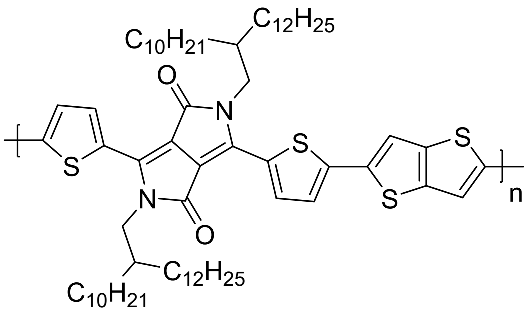


4 **TT** **3**

	Monomer Ratio			**Extraction Solvent**	**Yield (%)**	**Molecular Weight (KDa)**		**PDI**	λ_{max}^{soln} **(nm)**[b]	λ_{max}^{film} **(nm)**[c]
Polymer	**4**	**3**	**TT**			M_n[a]	M_w[a]			
PDPP-TTref	1	0	1	DCM	77	26.3	102.7	3.9	821	821
PDPP-TT5%	0.95	0.05	1	$CHCl_3$	83	24.4	79.1	3.2	810	812
PDPP-TT10%	0.90	0.1	1	CB	71	78.4	221.2	2.8	812	813
PDPP-TT20%	0.80	0.2	1	$CHCl_3$	39	14.0	76.4	5.5	804	802

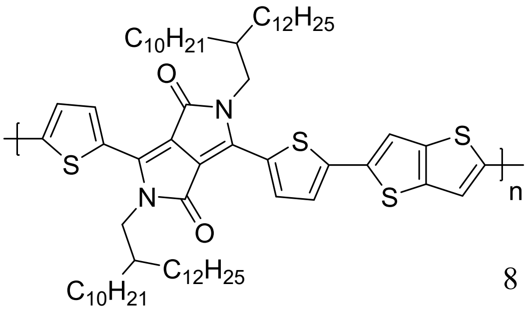
[a]Determined by GPC (CB) against PS standard; [b]CB solution; [c]Spin coated from CB (5 mg/mL).

Synthesis of PDPP-TTref



To an oven dried 10 mL microwave vial under argon was added **4** (0.10 g, 0.088 mmol), 2,5-bis(trimethylstannyl)-thieno[3,2-*b*]thiophene (0.041 g, 0.088 mmol), $Pd_2(dba)_3$ (0.003 g, 0.003 mmol) and $P(o\text{-tol})_3$ (0.003 g, 0.011 mmol). The reaction vial was then sealed and left to degas for 1 h. This was followed by the addition of degassed toluene (4.70 mL) and degassed DMF (0.47 mL). The reaction was then heated to 115 °C and allowed to stir for 18 h. The vial was then left to cool to RT and the reaction mixture was then added dropwise into a flask of stirring methanol. Precipitate (blue stringy flakes) began to form and was filtered into a cellulose thimble under reduced pressure, which was then washed with acetone and methanol. The polymer was then purified *via* Soxhlet extraction in the following solvents: acetone (12 h), hexane (12 h) and dichloromethane (12 h). The dichloromethane fraction was then concentrated *in vacuo* to give a deep blue plastic-like film. The solid was dissolved in minimum chlorobenzene and added dropwise slowly into a flask of rapidly stirring methanol. Once the addition was completed, the mixture was allowed to stir for a further 30 min before the dark blue solid was collected *via* filtration and washed with methanol and acetone, to afford the dark blue polymer **PDPP-TTref** (0.07 g, 77%); M_n: 26.3 KDa; M_w: 102.7 KDa; PDI: 3.9.

*Synthesis of PDPP-TT*5%



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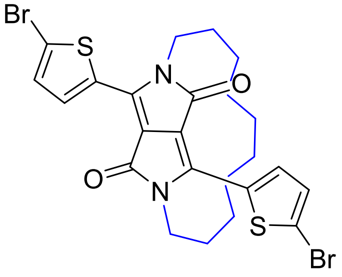
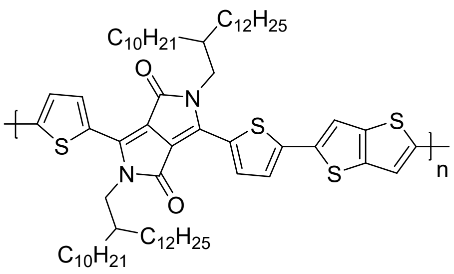


5%

PDPP-TT5% was made *via* the same procedure as **PDPP-TTref**, with the following amounts of reagents; **4** (0.10 g, 0.088 mmol), **3** (2.8 mg, 0.005 mmol) and 2,5-bis(trimethylstannyl)-thieno[3,2-*b*]thiophene (0.043 g, 0.093 mmol). The polymer was then purified *via* Soxhlet extraction in the following solvents: acetone (12 h), hexane (12 h), dichloromethane (12 h) and chloroform (12 h). The chloroform fraction was then concentrated *in vacuo* to give a deep blue plastic-like film. The solid was dissolved in minimum chlorobenzene and added dropwise slowly into a flask of rapidly stirring methanol. Once the addition was completed, the mixture was allowed to stir for a further 30 min before the dark blue solid was collected *via* filtration and washed with methanol and acetone, to afford the dark blue polymer **PDPP-TT5%** (0.08 g, 83%); M_n: 24.4 KDa; M_w: 79.1 KDa; PDI: 3.2.



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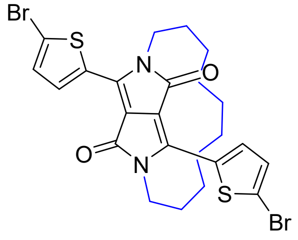
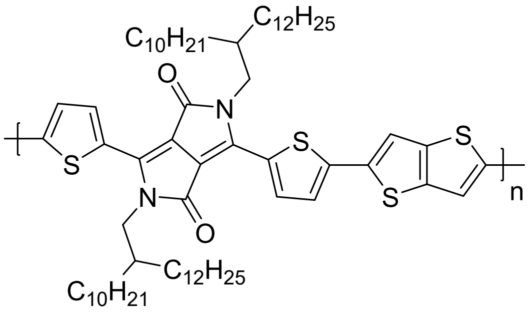


10%

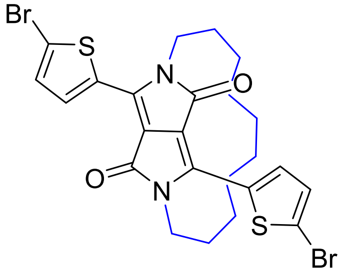
Synthesis of PDPP-TT10%

PDPP-TT10% was made *via* the same procedure as **PDPP-TTref**, with the following amounts of reagents; **4** (0.10 g, 0.088 mmol), **3** (5.9 mg, 0.010 mmol) and 2,5-bis(trimethylstannyl)-thieno[3,2-*b*]thiophene (0.046 g, 0.098 mmol). The polymer was then purified *via* Soxhlet extraction in the following solvents: acetone (12 h), hexane (12 h), dichloromethane (12 h), chloroform (12 h) and chlorobenzene (12 h). The chlorobenzene fraction was then concentrated *in vacuo* to give a deep blue plastic-like film. The solid was dissolved in minimum chlorobenzene and added dropwise slowly into a flask of rapidly stirring methanol. Once the addition was completed, the mixture was allowed to stir for a further 30 min before the dark blue solid was collected *via* filtration and washed with methanol and acetone, to afford the dark blue polymer **PDPP-TT10%** (0.07 g, 71%); M_n: 78.4 KDa; M_w: 221.2 KDa; PDI: 2.8.

Synthesis of PDPP-TT20%



3

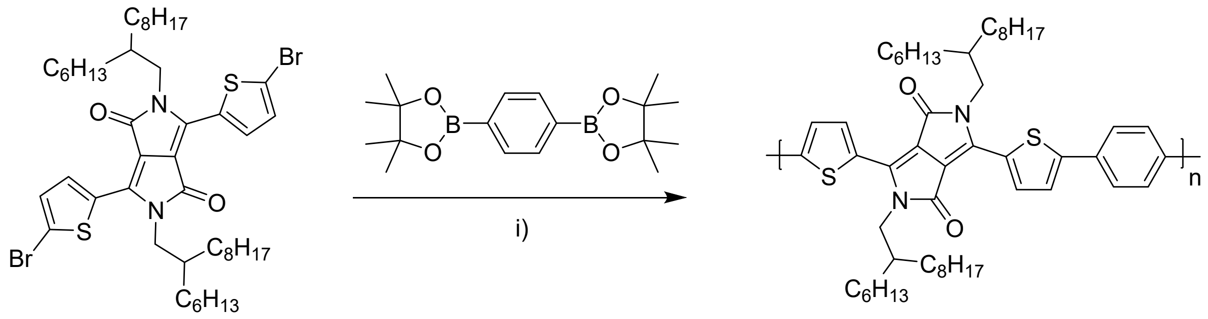


20%

PDPP-TT20% was made *via* the same procedure as **PDPP-TTref**, with the following amounts of reagents; **4** (0.10 g, 0.088 mmol), **3** (13.2 mg, 0.022 mmol) and 2,5-bis(trimethylstannyl)-thieno[3,2-*b*]thiophene (0.051 g, 0.110 mmol). The polymer was then purified *via* Soxhlet extraction in the following solvents: acetone (12 h), hexane (12 h), dichloromethane (12 h) and chloroform (12 h). The chloroform fraction was then concentrated *in vacuo* to give a deep blue plastic-like film. The solid was dissolved in minimum chlorobenzene and added dropwise slowly into a flask of rapidly stirring methanol. Once the addition was completed, the mixture was allowed to stir for a further 30 min before the dark blue solid was collected *via* filtration and washed with methanol and acetone, to afford the dark blue polymer **PDPP-TT20%** (0.05 g, 39%); M_n: 14.0 KDa; M_w: 76.4 KDa; PDI: 5.5.

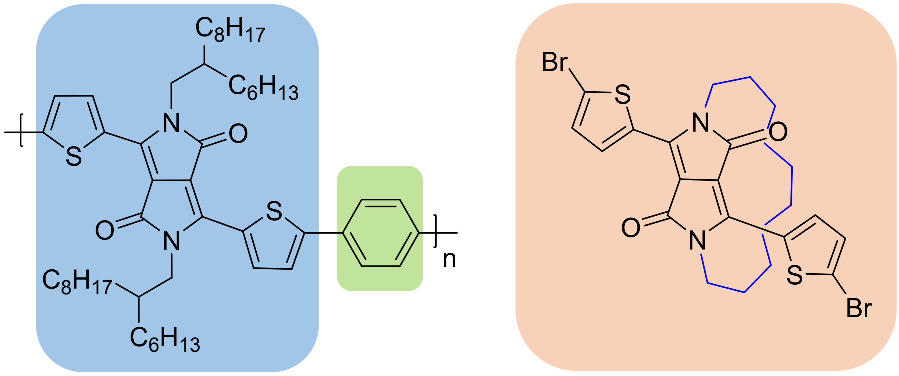
Synthesis of the DPP polymers – P Series

Reference Polymer **PDPP-Pref**



5 **PDPP-Pref**

Table S2. A summary of the monomer ratios, extraction solvents used to isolate the DPP polymers, yields, molecular weights, PDI and optical properties of the polymers in the study.

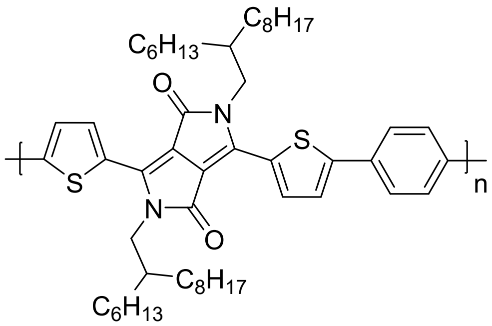


5 **P** **3**

	Monomer Ratio			Extraction Solvent	Yield (%)	Molecular Weight (KDa)		PDI	λ_{max}^{soln} (nm)[b]	λ_{max}^{film} (nm)[c]
Polymer	**5**	**3**	**TT**			M_n[a]	M_w[a]			
PDPP-Pref	1	0	1	CB	77	25.1	72.7	2.9	756	760
PDPP-P5%	0.95	0.05	1	CB	54	28.4	86.1	3.0	752	757
PDPP-P10%	0.90	0.1	1	CB	64	25.1	79.5	3.2	749	750

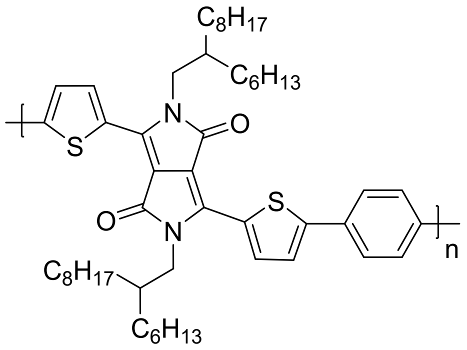
[a]Determined by GPC (1,2,4-trichlorobenzene) against PS standard; [b]CB solution; [c]Spin coated from CB (5 mg/mL).

Synthesis of PDPP-Pref

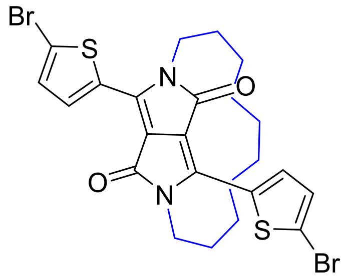


To a 10 mL oven dried microwave vial under argon was added **5** (0.10 g, 0.11 mmol), 1,4-benzenediboronic acid bis(pinacol) ester (0.036 g, 0.11 mmol), triphenylphosphine (3.10 mg, 0.0117 mmol) and tris(dibenzylideneacetone)dipalladium (0) (4.55 mg, 0.0050 mmol). The reaction vial was then sealed and left to degas for 1 h. This was followed by the addition of degassed toluene (1.81 mL) containing a few drops of Aliquat 336 and degassed K_3PO_4 aq solution (0.23 mL) made from a stock solution (0.99 g of K_3PO_4 in 2.3 mL water). The reaction was then heated to 115 °C and allowed to stir for 3 days. The vial was then left to cool to RT and the reaction mixture was then added dropwise into a flask of stirring methanol. Precipitate (blue stringy flakes) began to form and was filtered into a cellulose thimble under reduced pressure, which was then washed with acetone and methanol. The polymer was then purified *via* Soxhlet extraction in the following solvents: acetone (12 h), hexane (12 h) and chloroform (12 h). The chloroform fraction was then concentrated *in vacuo* to give a deep blue plastic-like film. The solid was dissolved in minimum chlorobenzene and added dropwise slowly into a flask of rapidly stirring methanol. Once the addition was completed, the mixture was allowed to stir for a further 30 min before the dark blue solid was collected *via* filtration and washed with methanol and acetone, to afford the dark blue polymer **PDPP-Pref** (0.07 g, 77%); M_n: 25.1 KDa; M_w: 72.7 KDa; PDI: 2.9.

Synthesis of PDPP-P5%



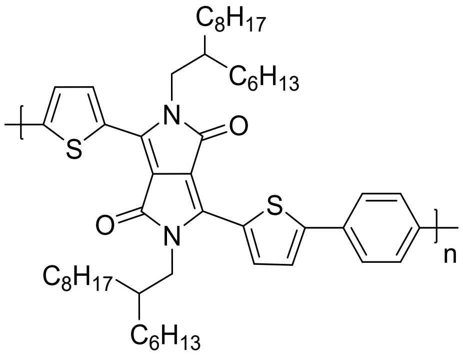
3



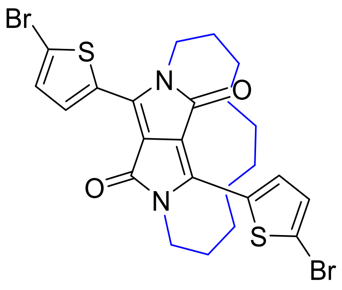
5 %

PDPP-P5% was made *via* the same procedure as **PDPP-Pref**, with the following amounts of reagents; **5** (0.10 g, 0.110 mmol), **3** (3.5 mg, 0.006 mmol), 1,4-benzenediboronic acid bis(pinacol) ester (0.038 g, 0.116 mmol). The polymer was then purified *via* Soxhlet extraction in the following solvents: acetone (12 h), hexane (12 h), chloroform (12 h) and chlorobenzene (12 h). The chlorobenzene fraction was then concentrated *in vacuo* to give a deep blue plastic-like film. The solid was dissolved in minimum chlorobenzene and added dropwise slowly into a flask of rapidly stirring methanol. Once the addition was completed, the mixture was allowed to stir for a further 30 min before the dark blue solid was collected *via* filtration and washed with methanol and acetone, to afford the dark blue polymer **PDPP-P5%** (0.05 g, 54%); M_n: 28.4 KDa; M_w: 86.1 KDa; PDI: 3.0.

Synthesis of PDPP-P10%



3



10 %

PDPP-P10% was made *via* the same procedure as **PDPP-Pref**, with the following amounts of reagents; **5** (0.09 g, 0.099 mmol), **3** (6.5 mg, 0.011 mmol), 1,4-benzenediboronic acid bis(pinacol) ester (0.036 g, 0.110 mmol). The polymer was then purified *via* Soxhlet extraction in the following solvents: acetone (12 h), hexane (12 h), chloroform (12 h) and chlorobenzene (12 h). The chlorobenzene fraction was then concentrated *in vacuo* to give a deep blue plastic-like film. The solid was dissolved in minimum chlorobenzene and added dropwise slowly into a flask of rapidly stirring methanol. Once the addition was completed, the mixture was allowed to stir for a further 30 min before the dark blue solid was collected *via* filtration and washed with methanol and acetone, to afford the dark blue polymer **PDPP-P10%** (0.06 g, 64%); M_n: 25.1 KDa; M_w: 79.5 KDa; PDI: 3.2.

4. Single Crystal X-Ray Diffraction Studies

Single-crystal X-ray diffraction data were collected on a Bruker D8-QUEST diffractometer, equipped with an Incoatec IμS Cu microsource (λ = 1.5418 Å) and a PHOTON-100 detector operating in shutterless mode. The temperature was controlled by an Oxford Cryosystems open-flow N_2 Cryostream operating at 180(2) K. The control and processing software was Bruker *APEX*3. The diffraction images were integrated using *SAINT* in *APEX*3 to a resolution of 0.84 Å, and a multi-scan correction was applied using *SADABS*. The final unit-cell parameters were refined against all reflections over the full data range. The structure was solved using *SHELXT* [G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8] and refined using *SHELXL* [G. M. Sheldrick, Acta Cryst., 2015, C71, 3-8]. All non-H atoms were refined with anisotropic displacement parameters. H atoms were placed in calculated positions and allowed to ride during subsequent refinement. Mercury [Macrae et al., J. Appl. Cryst. 2006, 39, 453-457] was used to visualise and analyse the crystal structures.

Compound 2. HB_B1_0003: The alkyl chain shows partial disorder, which was modelled as two components for atoms C17 and C18. All C—C distances along the chain were restrained to 1.54 Å and the ADPs of the partially occupied atoms C17/C17A and C18/C18A were restrained to resemble isotropic behaviour (ISOR in *SHELXL*). Aside from this partial disorder, the molecule retains approximate C_2 point symmetry, with the 2-fold axis passing through the centre of the DPP group and the midpoint of the central C—C bond in the alkyl chain.

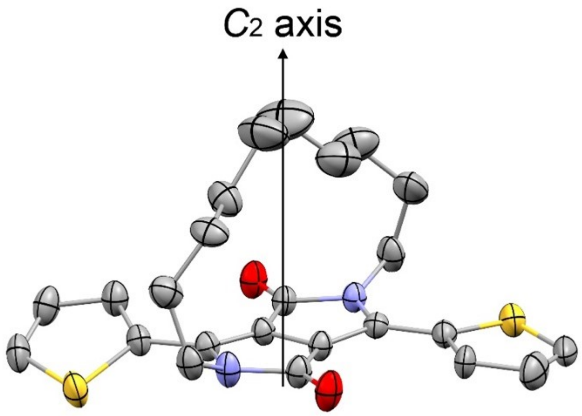


Figure S1: Crystal structure of compound 2. Minor disorder component of the alkyl chain not shown

Compound 3. HB_B1_0008: Structure refinement was straightforward.

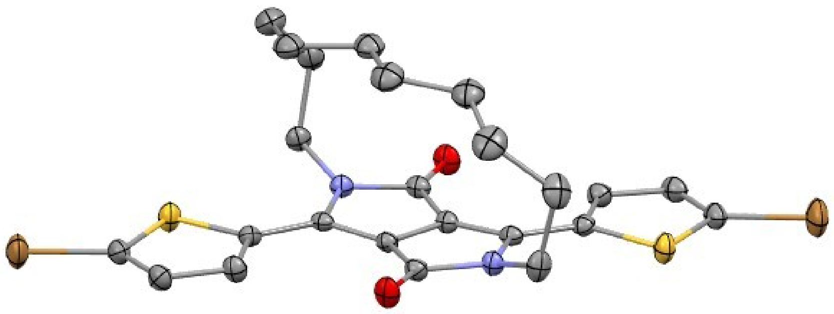


Figure S2: Crystal structure of compound 3.

Table S3. Summary of crystallographic information

	2	**3**
CCDC number	2164409	2177219
Cambridge data number	HB_B1_0003	HB_B1_0008
Chemical formula	$C_{24}H_{26}N_2O_2S_2$	$C_{24}H_{24}Br_2N_2O_2S_2$
Formula weight	438.59	596.39
Temperature / K	180(2)	180(2)
Crystal system	monoclinic	triclinic
Space group	*C*2/*c*	*P*–1
a / Å	28.3920(9)	10.0631(3)
b / Å	8.9830(3)	10.1990(4)
c / Å	19.2814(6)	11.4730(4)
/ °	90	95.6730(14)
/ °	117.135(2)	98.5888(12)
/ °	90	92.6598(13)
Unit-cell volume / Å^3	4376.4(3)	1156.37(7)
Z	8	2
Calc. density / g cm^{-3}	1.331	1.713

F(000)	1856	600
Radiation type	Cu Kα	Cu Kα
Absorption coefficient / mm^{-1}	2.389	6.342
Crystal size / mm^3	0.22 x 0.15 x 0.06	0.15 x 0.08 x 0.04
2θ range / °	7.00-133.66	7.84-133.87
Completeness to max 2θ	0.998	0.993
No. of reflections measured	19770	13431
No. of independent reflections	3887	4095
R(int)	0.0429	0.0266
No. parameters / restraints	290 / 36	290 / 0
Final R1 values ($I > 2\sigma(I)$)	0.0547	0.0231
Final wR(F^2) values (all data)	0.1547	0.0584
Goodness-of-fit on F^2	1.063	1.050
Largest difference peak & hole / e Å^{-3}	0.761, -0.376	0.336, -0.295

5. UV-Visible Spectra (P-Series)

Solution

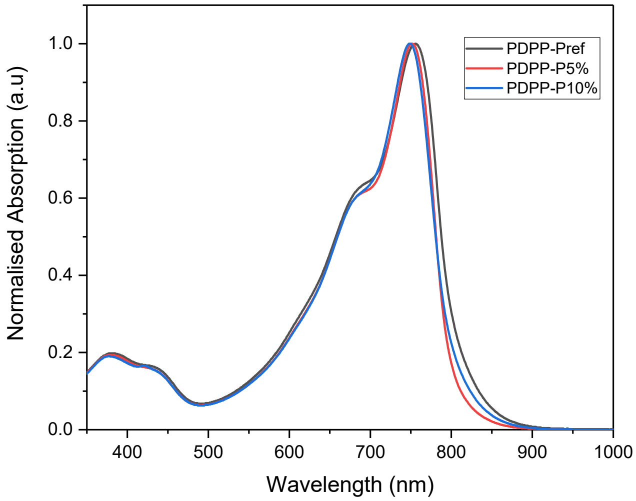


Figure S3: Normalized solution (CB) UV-vis absorption for reference polymer (PDPP-Pref) and encapsulated polymers (PDPP-P5% and PDPP-P10%).

Thin Film

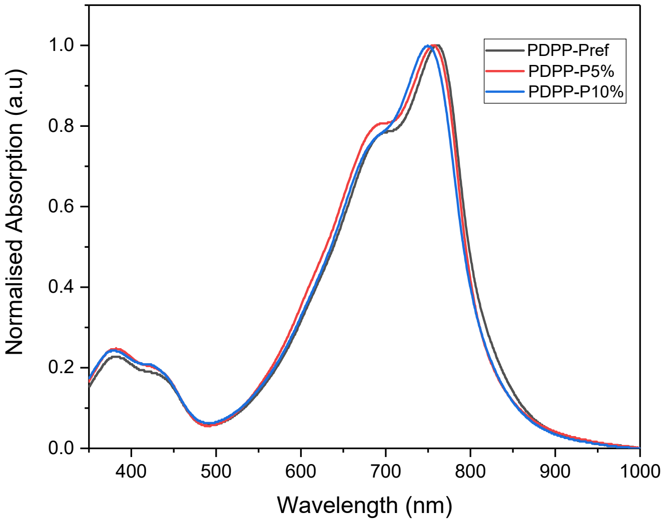


Figure S4: Normalized thin film (spin coated from CB 5 mg/mL) UV-vis absorption for reference polymer (PDPP-Pref) and encapsulated polymers (PDPP-P5% and PDPP-P10%).

6. ^{1}H NMR Spectra

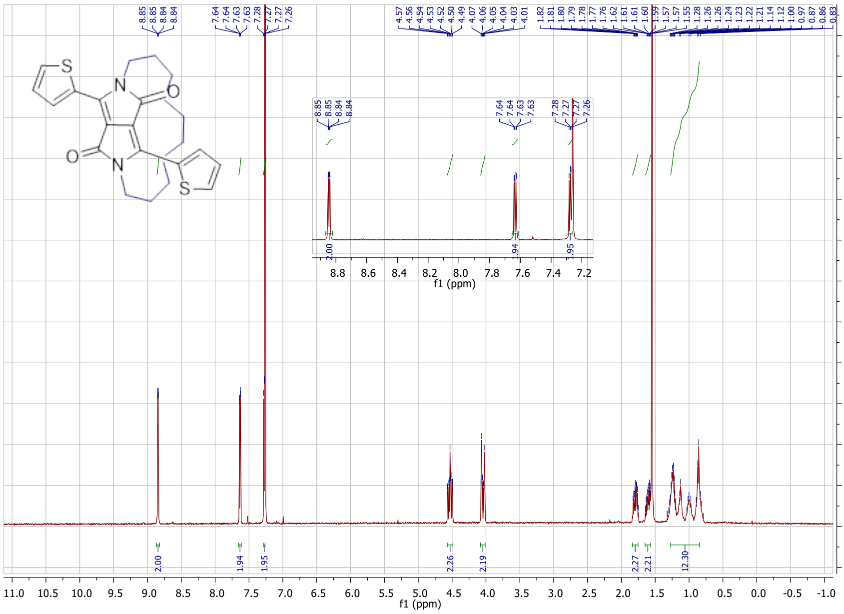


Figure S5. ^{1}H NMR spectrum of Compound **2**

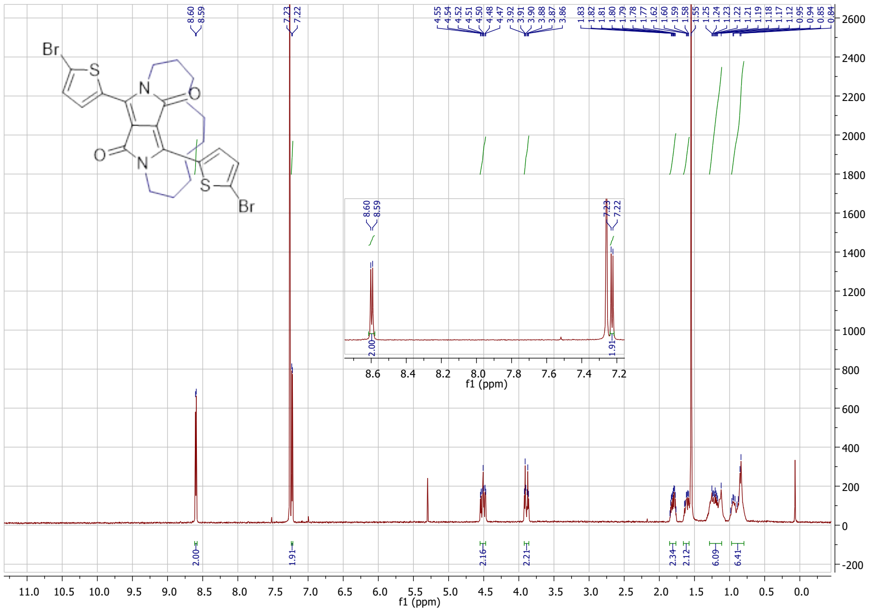


Figure S6. ^{1}H NMR spectrum of Compound **3**

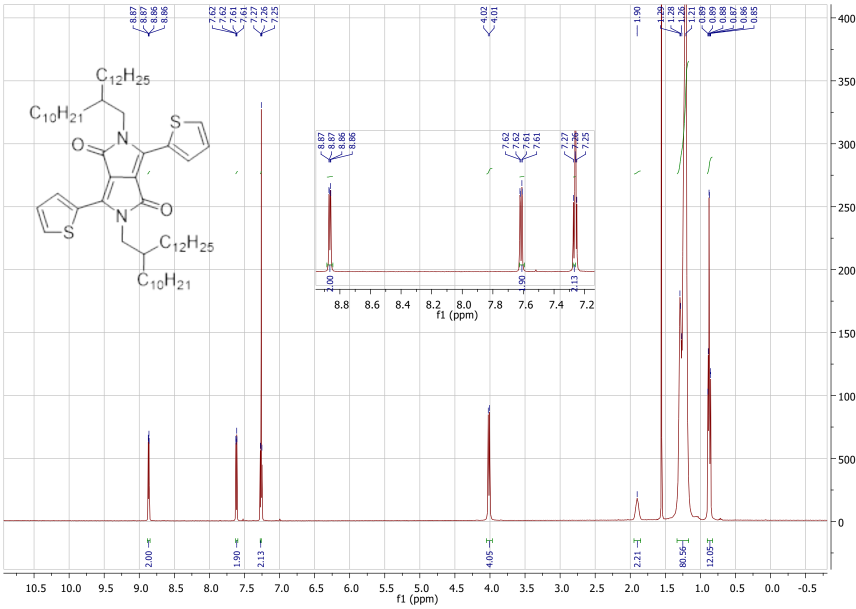


Figure S7. ^{1}H NMR spectrum of 2,5-bis(2-decyltetradecyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**DT-Alkylated DPP**)

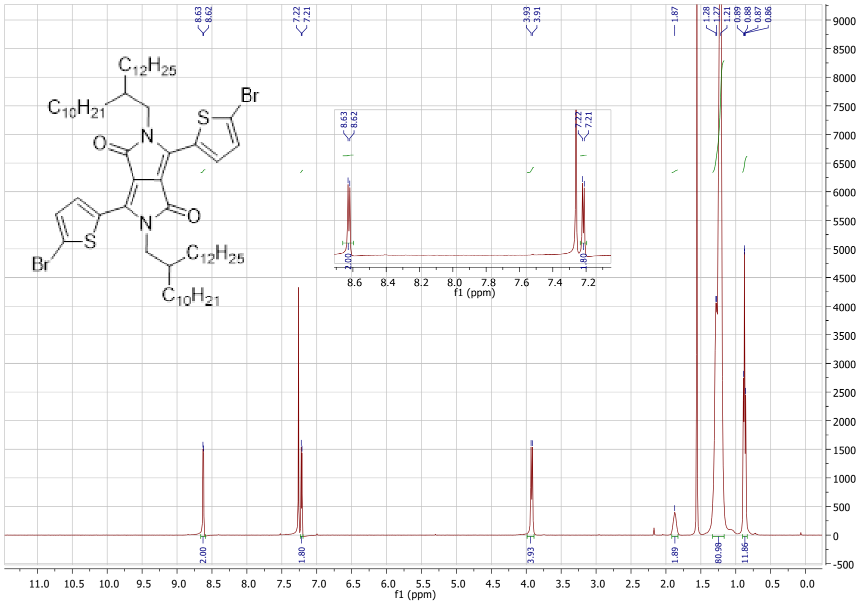


Figure S8. ^{1}H NMR spectrum of Compound **4**

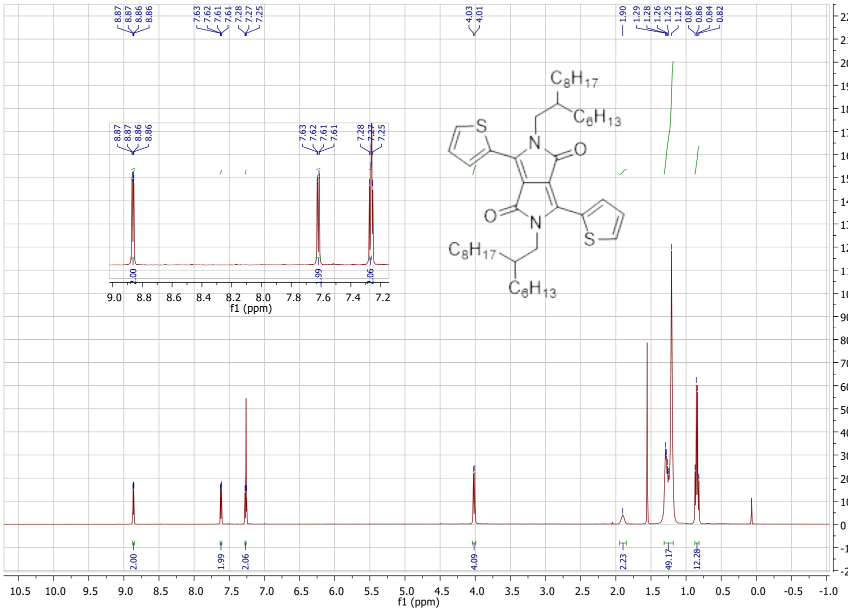


Figure S9. ^{1}H NMR spectrum of 2,5-bis(2-hexyldecyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**HD-Alkylated DPP**)

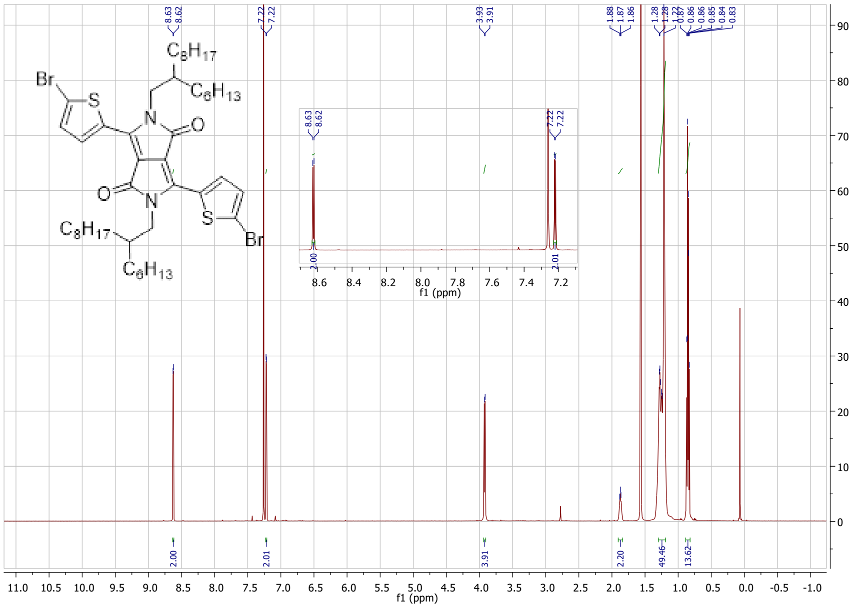


Figure S10. ^{1}H NMR spectrum of Compound **5**

6. ^{13}C NMR Spectra

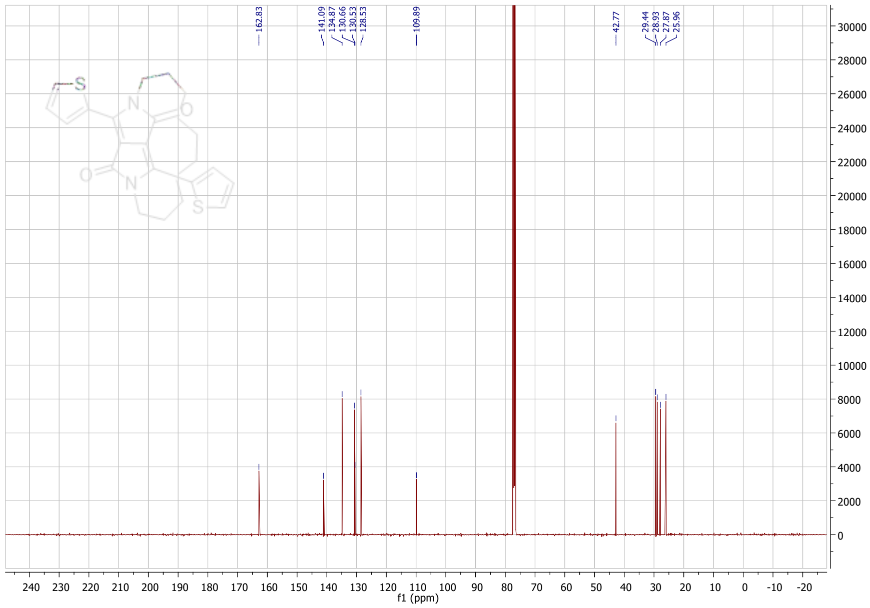


Figure S11. ^{13}C NMR spectrum of Compound **2**

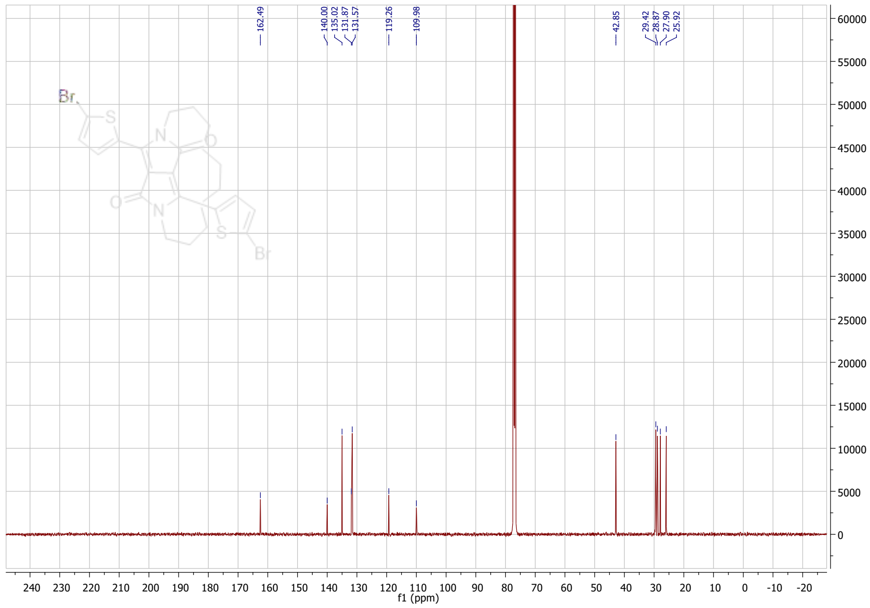


Figure S12. ^{13}C NMR spectrum of Compound **3**

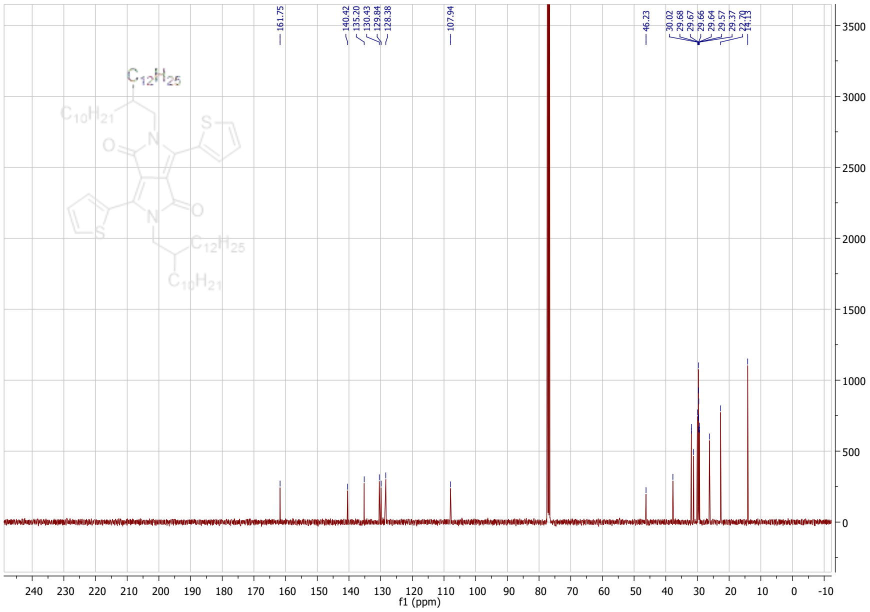


Figure S13. ^{13}C NMR spectrum of 2,5-bis(2-decyltetradecyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**Alkylated DPP**)

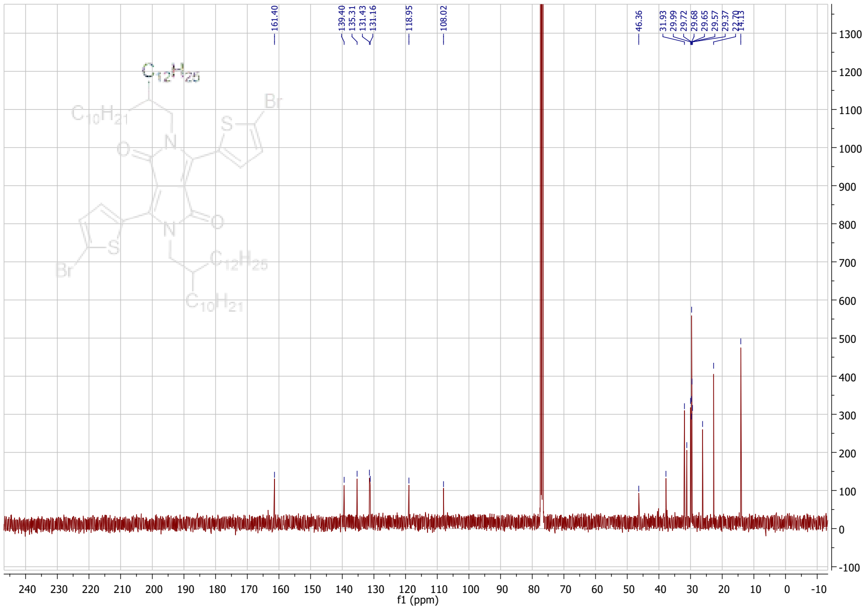


Figure S14. ^{13}C NMR spectrum of Compound **4**

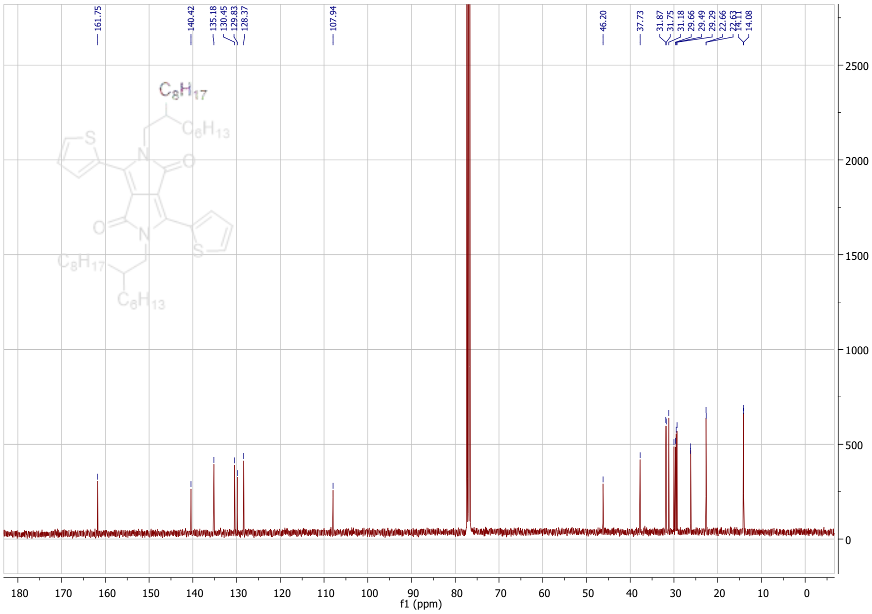


Figure S15. ^{13}C NMR spectrum of 2,5-bis(2-hexyldecyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**HD-Alkylated DPP**)

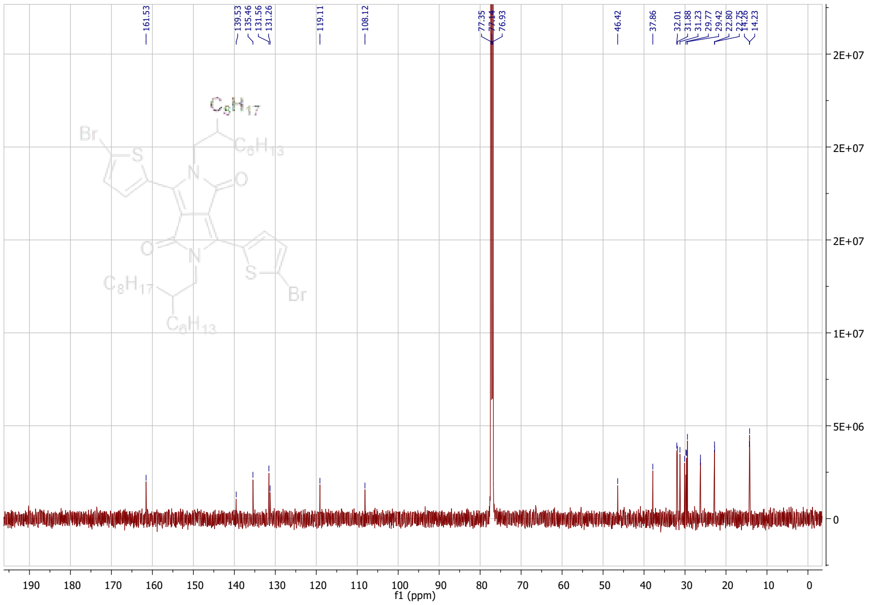


Figure S16. ^{13}C NMR spectrum of Compound **5**

7. Device Characterization

PDPP-TT based OSCs

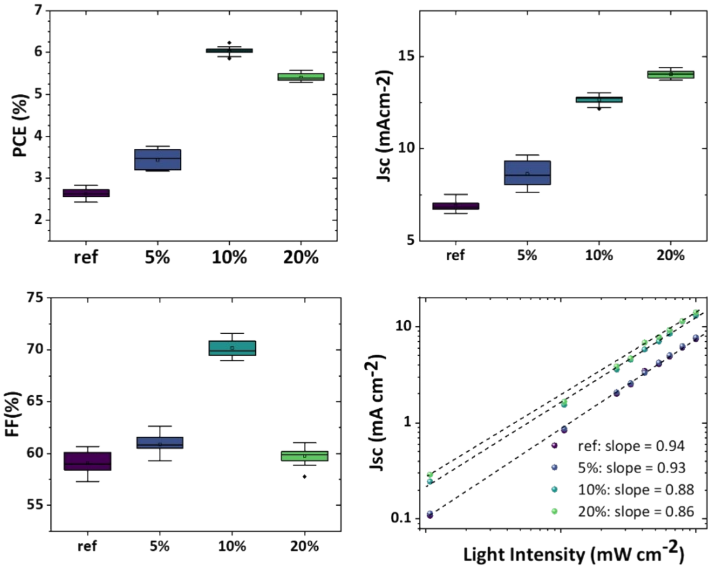


Figure S17: Box plots demonstrating the statistical variation in the J-V parameters of PDPP-TT: PC$_{71}$BM BHJ solar cells with different PDPP-TT polymer analogs. The lower right plot shows the intensity depended on the Jsc of the devices.

HD-PDPP-P based OSCs

Devices with the structure ITO/PEDOT: PSS/BHJ/DPO/Ag were fabricated following the same procedure as in the case of PDPP-TT counterparts. For these devices, the active layer was deposited from a chloroform solution (3 volume % diphenyl ether as solvent additive) of polymer: PC$_{71}$BM (1:2 v/v) at 3000 rpm for 60 sec, to result in films of ~ 120 nm.

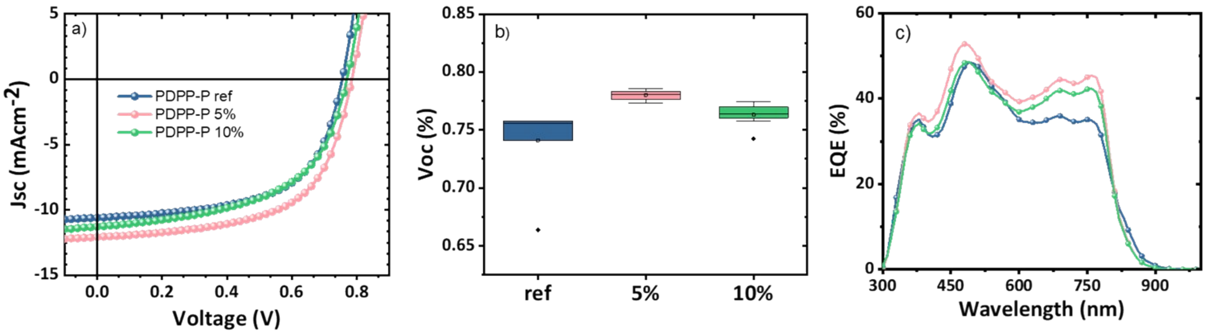


Figure S18: a) J-V characteristics b) box plot depicting the statistical distribution of Voc calculated over at least six devices and c) and EQE of OSCs based on the polymer: PC$_{71}$BM BHJ blends using different HD-PDPP-P polymer analogs.

Table S4: Summary of J-V parameters of OSCs fabricated using donor polymers based on PDPP-P analogs with varying fractions of encapsulated units. The Jsc values are corrected using the integrated Jsc from EQE.

PDPP-P	**Jsc (mAcm^{-2})**	**Voc (V)**	**FF (%)**	**PCE$_{max}$ (%)**
Ref	10.6	0.75	60	4.7
5%	12.1	0.78	60	5.6
10%	11.3	0.77	55	4.7

8. Voltage loss quantification

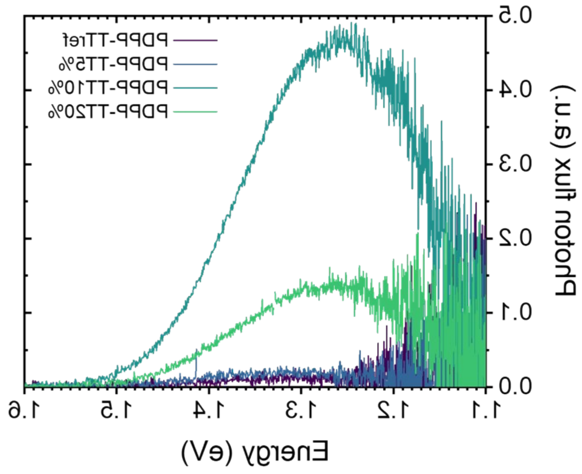


Figure S19a: EL spectra (corrected for detector sensitivity) of polymer-PC$_{71}$BM BHJ devices with different polymer analogs as the donor material.

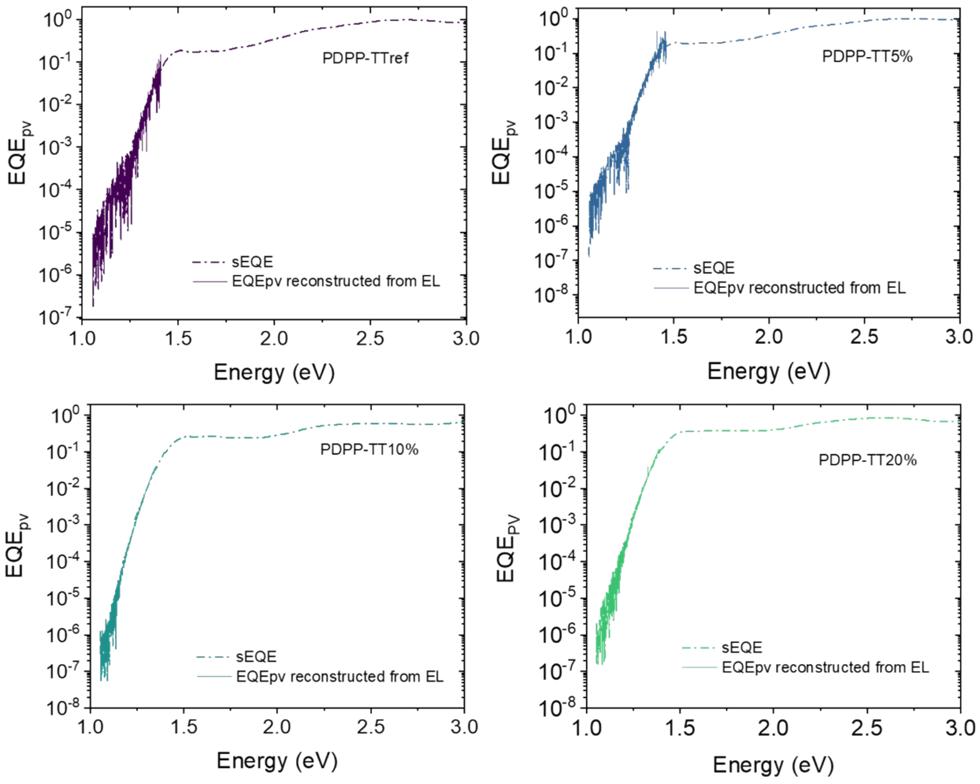


Figure S19b: Quantum efficiency measured by sensitive EQE and EQE$_{pv}$ evaluated from the EL spectra and blackbody radiation using the reciprocity relationship of polymer: PC$_{71}$BM BHJ devices based on polymer analogs a) PDPP-TTref b) PDPP-TT5%, PDPP-TT10%, and d) PDPP-TT20%.

9. Photothermal Deflection Spectroscopy (PDS)

In the PDS measurements presented in Figure 4a of the manuscript, the slit width was reduced to 0.5 mm. Hence, a spectral resolution of around 7.0 meV was achieved, as determined from the full-width-at-half-maximum of excitation light (Figure S20).

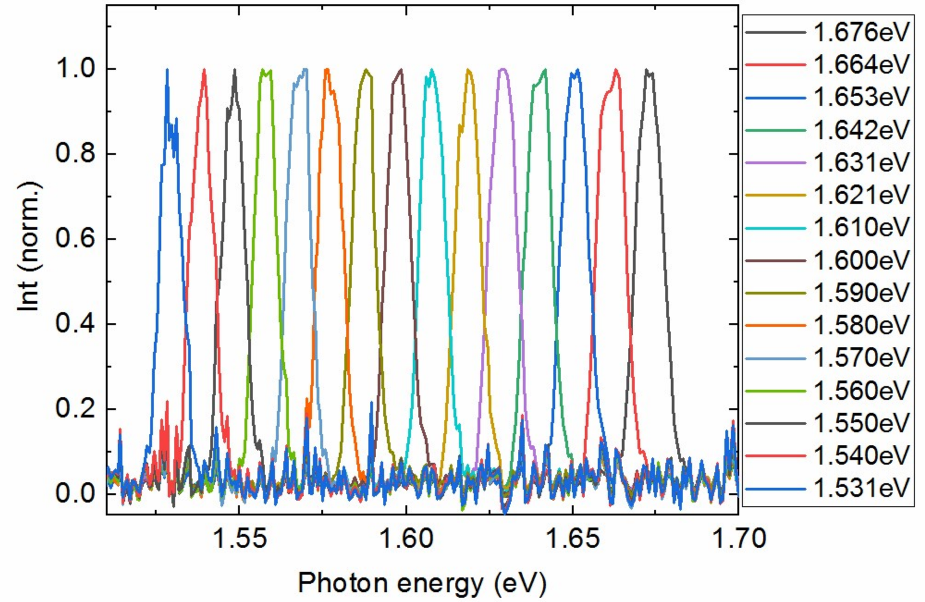


Figure S20: Spectral linewidth of representative excitation light energies used in the PDS experiments.

10. Atomic Force Microscopy (AFM)

Topographical images were recorded in semi-contact mode using Next-Solve by MD-NDT with TESP-SS cantilevers (Bruker) with a tip radius of ~ 2 nm.

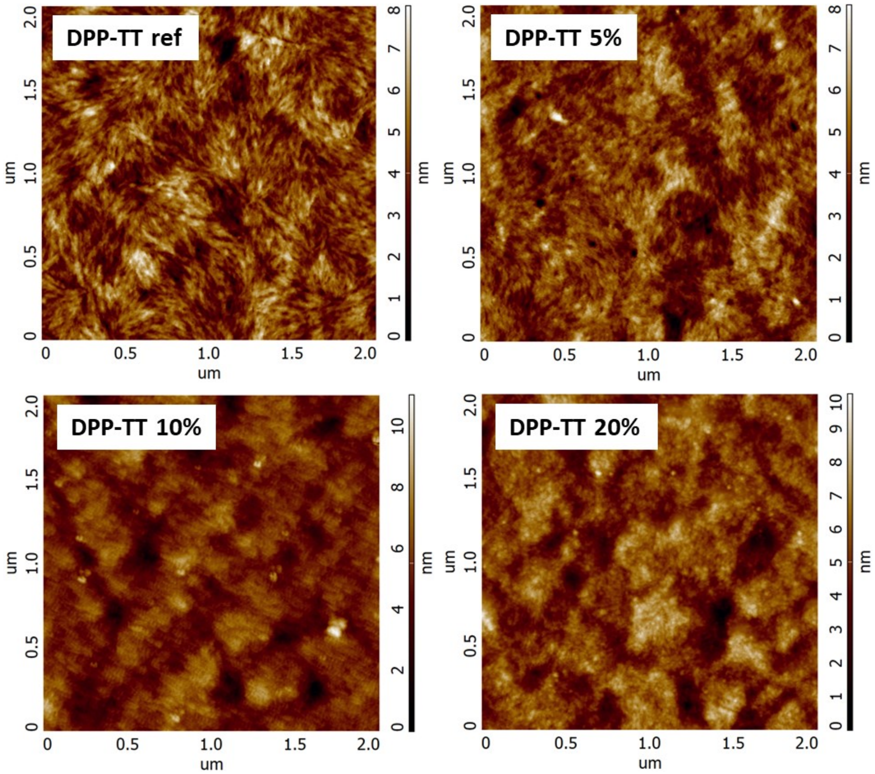


Figure S21a: Surface topography of neat films of PDPP-TT analogs

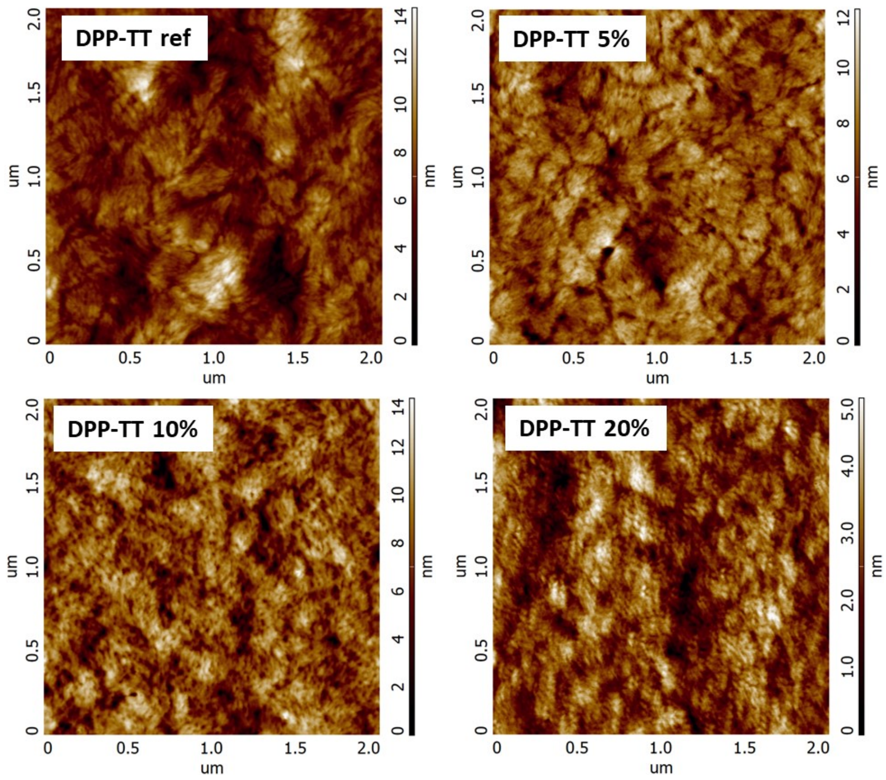


Figure S21b: Surface topography of BHJ blend films with PDPP-TT analogs

11. Grazing Incidence X-ray Diffraction (GIXRD)

GIXRD measurements were performed on D8 Discover (Bruker) equipment with a IμS CuKα source (λ = 1.54 Å) and an Eiger 2R 500K detector, at an incidence angle of 0.18°, collection time of the 2400s per frame with three frames per sample and a total of 2h per sample.

Table S5: Summary of d-spacing of the lamellar stacking of the 100 and 200 reflections and peak area in BHJ blend films of different polymer analogs.

Out of plane d-spacing				Peak Area		
	100Å	**200Å**		**100**	**200**	
PDPP-TTref	21.68111	10.87941	4.913806	0.15096	0.00628	0.03001
PDPP-TT5%	20.50715	10.51597	4.877113	0.09075	0.00977	0.02114
PDPP-TT10%	-	-	4.859423	-	-	0.0213
PDPP-TT20%	-	-	4.812968	-	-	0.02026

12. Organic Field Effect Transistors (OFET)

OFETs were fabricated in a bottom-contact top-gate architecture. Bare glass substrates were cleaned following the same procedure specified for ITO substrates. After oxygen plasma treatment, the substrates were transferred into a sputter chamber. 40 nm of gold was deposited through a stencil mask to pattern the source and drain electrodes W=1000 µm, L=30, 40, 50, 80, and 100 µm. The polymer active layer was spin-coated for 30 s at 1500 rpm from 5 g L^{-1} chlorobenzene stock solutions. CYTOP (CTL-809) was spin-coated for 30 s at 2500 rpm and annealed for 70 min at 50 ºC to achieve a ~900 nm dielectric layer. Finally, 40 nm of Al was thermally evaporated through a stencil mask to pattern the gate electrodes. The FET characteristics were measured using a probe station within an N_2 filled glove-box connected to a Keithley 4200-SCS.7.

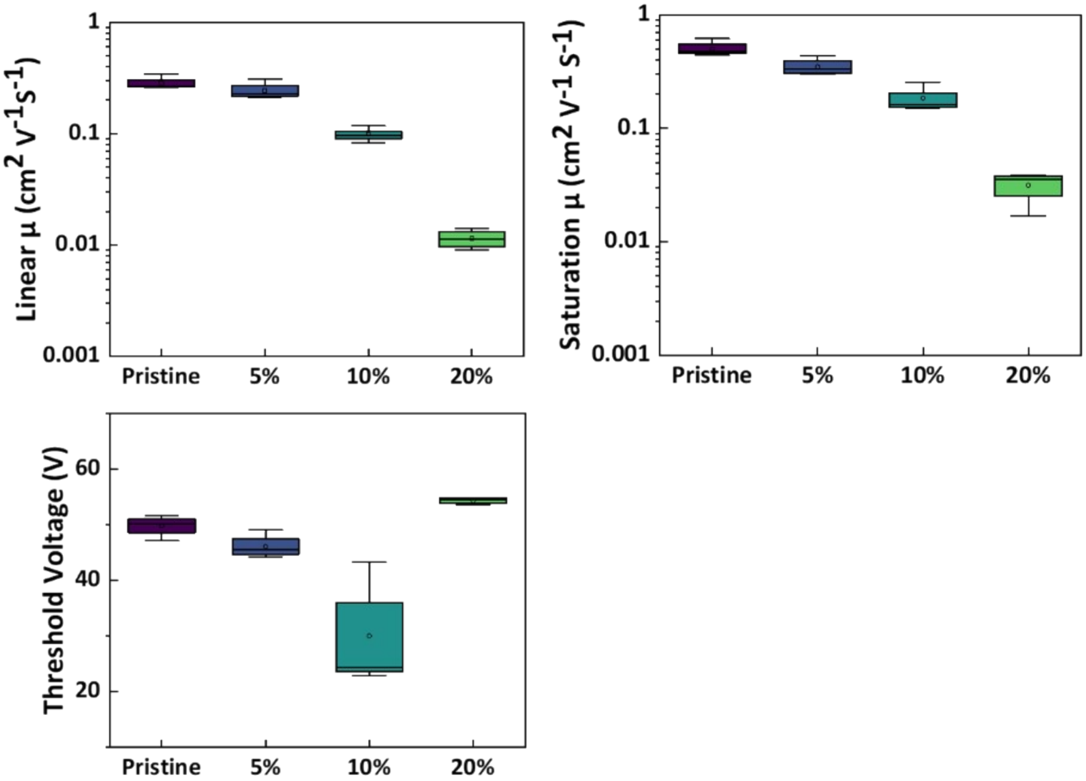


Figure S22: Plots showing the charge mobility of PDPP-TT polymer analogs measured in OFETs.

13. Photostability

The photostability of OSCs was measured using a home-built setup under inert conditions maintained with a constant flow of nitrogen. Devices were irradiated with one sun equivalent white light using a LED lamp and maintained at a temperature of under 38 °C using a cooling system. J-V parameters were tracked at regular intervals of time to follow the changes in the performance parameters over time.

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