

Supporting Information

Synthesis of Conjugated Polymers using Aryl-Bromides via Cu-Catalyzed Direct Arylation Polymerization (Cu- DArP)

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1. General

All reactions were performed under dry N₂ in oven dried glassware, unless otherwise noted. Unless otherwise noted, all reagents were purchased and used as received from commercial sources through VWR. Solvents were purchased from VWR and used without purification, unless otherwise noted. Cu(I) iodide (99.999%-Cu) PURATREM was purchased from Strem Chemicals and used as received. 2,2',3,3',5,5',6,6'-Octafluorobiphenyl (**2**) was purchased from TCI and used as received. 5-(2-ethylhexyl)-4H-Thieno[3,4-c]pyrrole-4,6(5H)-dione and 5-(2-decyltetradecyl)-4H-Thieno[3,4-c]pyrrole-4,6(5H)-dione, and 5,5'-dibromo-2,2'-bithiophene (**5**) were prepared previously following reported procedures.^{1,2} K₃PO₄ and K₂CO₃ was ground into a fine powder and dried at 120 °C in a vacuum oven before use. Anhydrous N,N-dimethylacetamide (DMA) was purchased from Acros Organics and used as received. m-xylene and o-xylene were dried over CaH₂ and distilled onto activated molecular sieves (4 Å) prior to use.

All ¹H NMR were recorded at 25 °C using CDCl₃ on either a Varian Mercury 400 MHz, Varian VNMR-500 MHz, or a Varian VNMR-600 MHz. All spectra were referenced to CHCl₃ (7.26 ppm), unless otherwise noted. Number average molecular weight (M_n) and polydispersity (Đ) were determined by size exclusion chromatography (SEC) using a Viscotek GPC Max VE 2001 separation module and a Viscotek Model 2501 UV detector, with 70 °C HPLC grade 1,2-dichlorobenzene (*o*-DCB) as eluent at a flow rate of 0.6 mL/min on one 300 × 7.8 mm TSK-Gel GMHHR-H column (Tosoh Corp). The instrument was calibrated vs. polystyrene standards (1050–3,800,000 g/mol), and data were analysed using OmniSec 4.6.0 software. Polymer samples were dissolved in HPLC grade *o*-dichlorobenzene at a concentration of 0.5 mg ml⁻¹, stirred at 110-120 °C until dissolved, cooled to room temperature, and filtered through a 0.2 μm PTFE filter.

2. Additional optimization of Cu-DArP conditions and polymerization results

Table S1. Additional polymerization results for the synthesis of P1 (PDOF-OD) using Cu-DArP.

Entry	Cat. Mol ^a %	Ligand ^b	Base ^c	Solvent ^d	Time (hr.)	M _n (kDa) ^e , Đ ^e	Yield ^e (%)
1	50	1, 10-Phanthroline	K ₃ PO ₄	DMA/m-xylene (1:1)	16	22.0, 2.1	67
2	5	1, 10-Phanthroline	K ₃ PO ₄	DMA/m-xylene (1:1)	72	-	0

^a99.999%-Puratrem Cu(I) iodide was used as the copper source. ^bLigand loadings were 1:1 ratio to Cu(I) ^cAll polymerizations were conducted using 4 equivalence of base. ^dN,N-dimethylacetamide = DMA. All polymerizations were conducted in 0.5 M concentration at 140 °C. ^eDetermined for polymer products after purification.

Table S2. Optimization of Cu-DArP conditions for the synthesis of TPD-copolymers.

Entry	Polymer ^a	Cat. Mol ^b %	Solvent ^c	Concentration (M)	Base ^d	M _n (kDa) ^e , Đ ^e	Yield ^e (%)
1	P2	50	DMA	0.1	K ₂ CO ₃	-	0
2	P2	50	DMA/m-xylene (1:1)	0.1	K ₂ CO ₃	2.6, 1.6	32
3	P2	50	DMA/m-xylene (1:1)	0.4	K ₂ CO ₃	5.1, 1.6	46
4	P2	50	DMA/m-xylene (1:1)	0.4	K ₃ PO ₄	-	0
5	P3	50	DMA/m-xylene (1:1)	0.4	K ₂ CO ₃	8.5, 1.8	61
6	P4	50	DMA/m-xylene (1:1)	0.4	K ₂ CO ₃	10.4, 1.7	72

^aAbbreviation of polymers are referred to Scheme 3 in the main text. ^b99.999%-Puratrem Cu(I) iodide was used as the copper source. Ligand (Phanthroline) loadings were 1:1 ratio to Cu(I) iodide ^cAll polymerizations were conducted at 140 °C. ^dAll polymerizations were conducted using 4 equivalence of base. ^eDetermined for polymer products after purification.

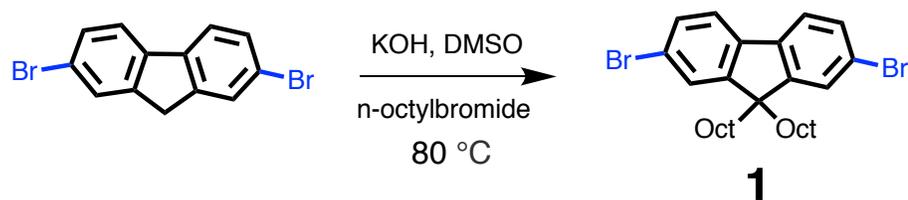
Detailed optimization process for the synthesis of TPD copolymers (Table S2):

As shown in Table S2 and Scheme 3, we initially focused on extending the optimized polymerization condition from our first report¹ to this study with aryl-bromide 1. This did not provide any reaction (Table S2, Entry 1), which indicates a much lower reactivity of aryl-bromides in Cu-DArP of TPD-copolymers, and is consistent with our observation from the synthesis of P1 (Table 1, Entry 1). Based on our study on the synthesis of P1 (PDOF-OD) (Table 1), we concluded that the DMA/m-xylene (1:1) co-solvent system is critical for Cu-DArP of aryl-bromides, therefore, we applied this methodology to the Cu-DArP of TPD-copolymers (Table S2, Entry 2), which led to P2 of M_n = 2.6 kDa, yield = 32%. Although an improved reaction outcome was

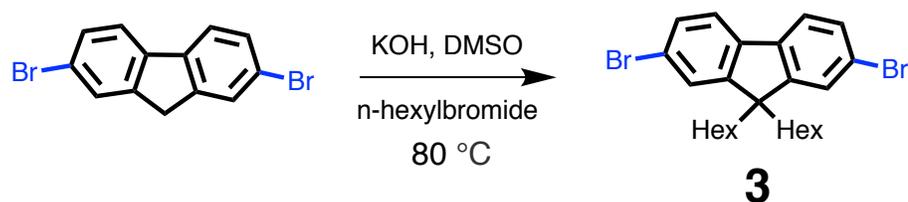
obtained, the low M_n and yield suggested that further optimization was required. Our previous study employed a diluted concentration (0.1 M) due to low solubilities of TPD-copolymers in polar amide solvent (DMA), however, conditions with higher concentration (>0.1 M) are much more favorable in step-growth polymerizations and are often utilized in DArP protocols.² Traditional DArP or Stille methodologies for the synthesis of TPD-copolymers are often conducted in non-polar solvents such as toluene, and with the introduction of a non-polar solvent (m-xylene), a much higher concentration (0.4 M) was employed for the synthesis of P2 (Table S2, Entry 3), which improved the M_n (5.1 kDa) and yield (46%). Replacement of K_2CO_3 with a stronger base K_3PO_4 (Table S2, Entry 4) completely prohibited the reaction.

Replacing octyl chains of the aryl-bromide 1 with hexyl substituted fluorene 3 effectively improved M_n (8.5 kDa) and yield (61%) (Table S2, Entry 5), and we postulate that hexyl side chains less sterically-hinder the copper catalyst center as a similar trend was found in our previous report.¹ To increase the solubility of polymer in the more concentrated solution, the 2-decyltetradecyl side chain was chosen to replace the 2-ethylhexyl chain attached to the TPD monomer, while keeping hexyl substituted fluorene 3 as the aryl-halide. This provides P4 with high M_n of 10.4 kDa and good yield 72% (Table S2, Entry 6), which is the highest M_n reported for TPD co-polymers synthesized via Cu-DArP.

3. Monomer Synthesis



9,9-Bis(octyl)-2,7-dibromofluorene (1). To a 100 mL 3-neck round-bottomed flask equipped with a stir bar under N_2 atmosphere, 2,7-dibromofluorene (1.0 equiv., 12.35 mmol, 4 g), KOH (6.0 equiv., 74.1 mmol, 4.16 g) were added and the 3-neck flask was vacuum backfilled three times, followed by addition of DMSO (30 mL) and n-octylbromide (3 equiv., 37.04 mmol, 7.15 g). The reaction was allowed to stir overnight at 80 °C. The reaction mixture was cooled down to room temperature, H_2O was then added (30 mL) and the mixture was extracted with hexanes three times. The organic layers were then washed with water, brine, and dried with $MgSO_4$. Purification was performed by column chromatography using hexanes as the eluent, and the solid was further purified by recrystallization using EtOH to obtain as a white solid (6.19 g, 87%). 1H NMR (500 MHz, Chloroform-*d*) δ 7.52 (d, $J = 7.9$ Hz, 2H), 7.45 (d, $J = 8.0$ Hz, 4H), 1.93 – 1.87 (m, 4H), 1.25 – 1.04 (m, 20H), 0.87 – 0.80 (m, 6H), 0.63 – 0.55 (m, 4H). Consistent with literature report.³



9,9-Bis(hexyl)-2,7-dibromofluorene (3). To a 50 mL 3-neck round-bottomed flask equipped with a stir bar under N_2 atmosphere, 2,7-dibromofluorene (1.0 equiv., 6.18 mmol, 2 g), KOH (6.0 equiv., 37.1 mmol, 2.08 g) were added and the 3-neck flask was vacuum backfilled three times, followed by addition of DMSO (20 mL) and n-hexylbromide (3 equiv., 18.52 mmol, 3.06 g). The reaction was allowed to stir overnight at 80 °C. The reaction mixture was cooled down to room temperature, H_2O was then added (20 mL) and the mixture was extracted with hexanes three times. The organic layers were then washed with water, brine, and dried with MgSO_4 . Purification was performed by column chromatography using hexanes as the eluent, and the solid was further purified by recrystallization using EtOH to obtain as a white solid (2.89 g, 90%). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.52 (d, $J = 7.9$ Hz, 2H), 7.46 (d, $J = 8.0$ Hz, 4H), 1.91 (m, 4H), 1.05 (m, 12H), 0.78 (m, 6H), 0.58 (m, 4H). Consistent with literature report.⁴



2,5-dibromothiophene (4). To a 50 mL 3-neck round-bottomed flask equipped with a stir bar under N_2 atmosphere, thiophene (1.0 equiv., 17.8 mmol, 1.5 g) and anhydrous DMF (20 mL) was added, followed by addition of N-bromosuccinimide (2.0 equiv., 36.5 mmol, 6.5 g) under protection from light. The mixture was allowed to stir at room temperature for 16 hours, and was poured in H_2O and extracted with Et_2O three times. The organic layers were then washed with water, brine, and dried with MgSO_4 . The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography using hexanes as the eluent. The product was then further purified via vacuum distillation to afford a colorless liquid (3 g, 70%). ^1H NMR (500 MHz, Chloroform-*d*) δ 6.84 (s, 2H). Consistent with literature report.⁵

4. Representative polymerization procedures

For P1 (PDOF-OD) (Table 1, Entry 6):

An oven-dried 15 mL high-pressure vessel equipped with a stir-bar was stoppered with a rubber-septum and cooled under a flow N₂. A stock solution of N,N-dimethylacetamide (DMA)/m-xylene (1:1) (0.25 mL DMA + 0.25 m-xylene) was mixed in a 10 mL 1-neck round-bottom-flask and degassed for 10 minutes. 9,9-bis(octyl)-2,7-dibromofluorene (**1**) (0.125 mmol, 1 equiv.), 2,2',3,3',5,5',6,6'-Octafluorobiphenyl (0.125 mmol, 1 equiv.), K₃PO₄ (4 equiv.), and phenanthroline (0.15 equiv) were added. The vessel was further sparged with N₂ (5 min.) followed by addition of DMA/m-xylene (1:1) stock solution (0.5 mL). CuI (0.15 equiv) was quickly added and the vessel sealed with a Teflon screw-cap. The vessel was then stirred at room temperature for 5 minutes. It was then submerged in a pre-heated oil bath with moderate stirring for 16 hours. The reaction was then cooled to room temperature, solids were dissolved in hot dichlorobenzene (3-5 mL), and the mixture was precipitated into a cold 10% (v:v) NH₄OH/methanol solution with high-stirring (100 mL). The grey precipitate was then collected via filtration, and it was washed with water, methanol, acetone, and hexanes several times yielding a brown/tan solid. The polymer was collected and dissolved in hot 1,2-dichlorobenzene (3-5 mL), precipitated into cold MeOH (100 mL), and filtered to yield an off-white/grey solid. It was then dried under high-vacuum overnight.

poly[(9,9-dioctylfluorene-2,7-diyl)-(2,2',3,3',5,5',6,6'-octafluoro-4,4'-diphenylene)] (PDOF-OD) (P1).
¹HNMR 500 MHz (CDCl₃): δ (ppm) 7.94 (br, 2H), 7.59 (br, 4H), 2.06 (br, 4H), 1.15 (br, 20H), 0.83 (br, 10H).
Consistent with literature report.⁶

For TPD-copolymers (P3) (Table S2, Entry 5):

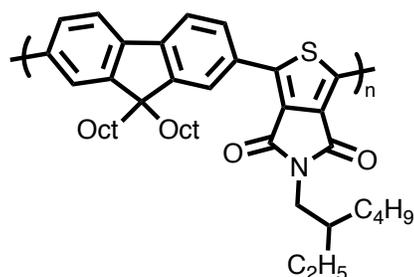
An oven-dried 15 mL high-pressure vessel equipped with a stir-bar was stoppered with a rubber-septum and cooled under a flow N₂. A stock solution of N,N-dimethylacetamide (DMA)/m-xylene (1:1) (0.32 mL DMA + 0.32 m-xylene) was mixed in a 10 mL 1-neck round-bottom-flask and degassed for 10 minutes. 9,9-bis(hexyl)-2,7-dibromofluorene (0.125 mmol, 1 equiv.), 5-(2-ethylhexyl)-4H-Thieno[3,4-c]pyrrole-4,6(5H)-dione (0.125 mmol, 1 equiv.), K₂CO₃ (4 equiv.), and phenanthroline (0.5 equiv) were added. The vessel was further sparged with N₂ (5 min.) followed by addition of DMA/m-xylene (1:1) stock solution (0.63 mL) to yield a 0.4 M concentration solution. CuI (0.5 equiv) was quickly added and the vessel sealed with a Teflon screw-cap. The vessel was then stirred at room temperature for 5 minutes. It was then submerged in a pre-heated oil bath with moderate stirring for 72 hours. The reaction was then cooled to room temperature, and was precipitated into a

cold 10% (v:v) NH_4OH /methanol solution with high-stirring (100 mL). The yellow precipitate was then collected via filtration, and it was washed with water, methanol, acetone, and hexanes several times yielding a yellow solid. The polymer was collected and dissolved in chloroform, concentrated down to ~ 1 mL, and re-precipitated into cold MeOH (100 mL), and filtered to yield a yellow solid. It was then dried under high-vacuum overnight.

For TPD-copolymers (P4) (Table 1, Entry 8):

An oven-dried 15 mL high-pressure vessel equipped with a stir-bar was stoppered with a rubber-septum and cooled under a flow N_2 . A stock solution of N,N-dimethylacetamide (DMA)/m-xylene (1:1) (0.32 mL DMA + 0.32 m-xylene) was mixed in a 10 mL 1-neck round-bottom-flask and degassed for 10 minutes. 9,9-bis(octyl)-2,7-dibromofluorene (0.125 mmol, 1 equiv.), 5-(2-decyltetradecyl)-4H-Thieno[3,4-c]pyrrole-4,6(5H)-dione (0.125 mmol, 1 equiv.), K_2CO_3 (4 equiv.), and phenanthroline (0.15 equiv) were added. The vessel was further sparged with N_2 (5 min.) followed by addition of DMA/m-xylene (1:1) stock solution (0.63 mL) to yield a 0.4 M concentration solution. CuI (0.15 equiv) was quickly added and the vessel sealed with a Teflon screw-cap. The vessel was then stirred at room temperature for 5 minutes. It was then submerged in a pre-heated oil bath with moderate stirring for 72 hours. The reaction was then cooled to room temperature, and was precipitated into a cold 10% (v:v) NH_4OH /methanol solution with high-stirring (100 mL). The yellow precipitate was then collected via filtration, and it was washed with water, methanol, and acetone several times yielding a yellow solid. The polymer was collected and dissolved in chloroform, concentrated down to ~ 1 mL, and re-precipitated into cold MeOH (100 mL), and filtered to yield a yellow solid. It was then dried under high-vacuum overnight.

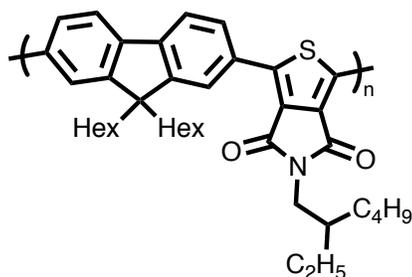
(Note: For P4, hexanes was not used for polymer washing because of high solubility of P4 in hexanes, even when M_n is high (presumably due to 2-decyltetradecyl chain on TPD monomer). P2, P3, P5, P6, however, were all collected after washing with hexanes during purifications.)



poly[(5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione-1,3-diyl)-alt-(9,9-dioctylfluorene2,7-diyl)]

(P2)

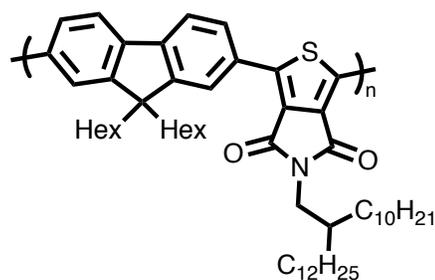
Yellow solid. ¹HNMR 500 MHz (CDCl₃): δ (ppm) 8.26-8.24 (m, 4H), 7.86 (d, 2H, J = 7.8 Hz), 3.65 (b, 2H), 2.17 (b, 4H), 1.93 (b, 1H), 1.56-1.34 (b, 8H), 1.20-1.12 (b, 20H), 0.98-0.92 (b, 6H), 0.82-0.68 (b, 10H).



poly[(5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione-1,3-diyl)-alt-(9,9-dihexylfluorene2,7-diyl)]

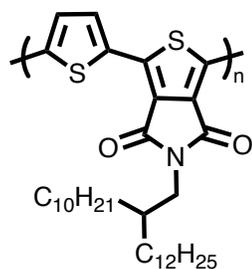
(P3)

Yellow solid. ¹HNMR 500 MHz (CDCl₃): δ (ppm) 8.27-8.23 (m, 4 H), 7.86 (d, 2H, J = 7.8 Hz), 3.65 (b, 2H), 2.17 (b, 4H), 1.92 (b, 1H), 1.54-1.34 (b, 8H), 1.14 (b, 12H), 0.98-0.93 (b, 6H), 0.78 (b, 10H).



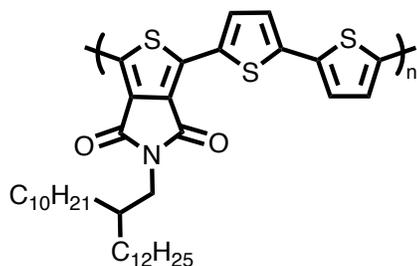
poly[(5-(2-decyltetradecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione-1,3-diyl)-alt-(9,9-dihexylfluorene2,7-diyl)] **(P4)**

Dark yellow solid. ¹HNMR 500 MHz (CDCl₃): δ (ppm) 8.28-8.21 (b, 4H), 7.786 (b, 2H), 3.62 (b, 2H), 2.16 (b, 4H), 1.97 (b, 1H), 1.41-1.10 (b, 52H), 0.87 (b, 6H), 0.79-0.69 (b, 10H).



poly[(5-(2-decyltetradecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione-1,3-diyl)-alt-(thiophene)] (P5)

Dark purple solid. ¹HNMR 500 MHz (CDCl₃): δ (ppm) 8.03 (b, 2H), 3.56 (b, 2H), 1.91 (b, 1H), 1.25 (b, 40 H), 0.86 (b, 6H).



poly[(5-(2-decyltetradecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione-1,3-diyl)-alt-(5,5'-dibromo-2,2'-bithiophene)] (P6)

Dark purple solid. ¹HNMR 500 MHz (CDCl₃): δ (ppm) 7.94 (b, 2H), 7.05 (b, 2H), 3.31 (b, 2H), 1.55 (b, 1H), 1.25 (b, 40 H), 0.86 (b, 6H).

5. NMR of Monomers

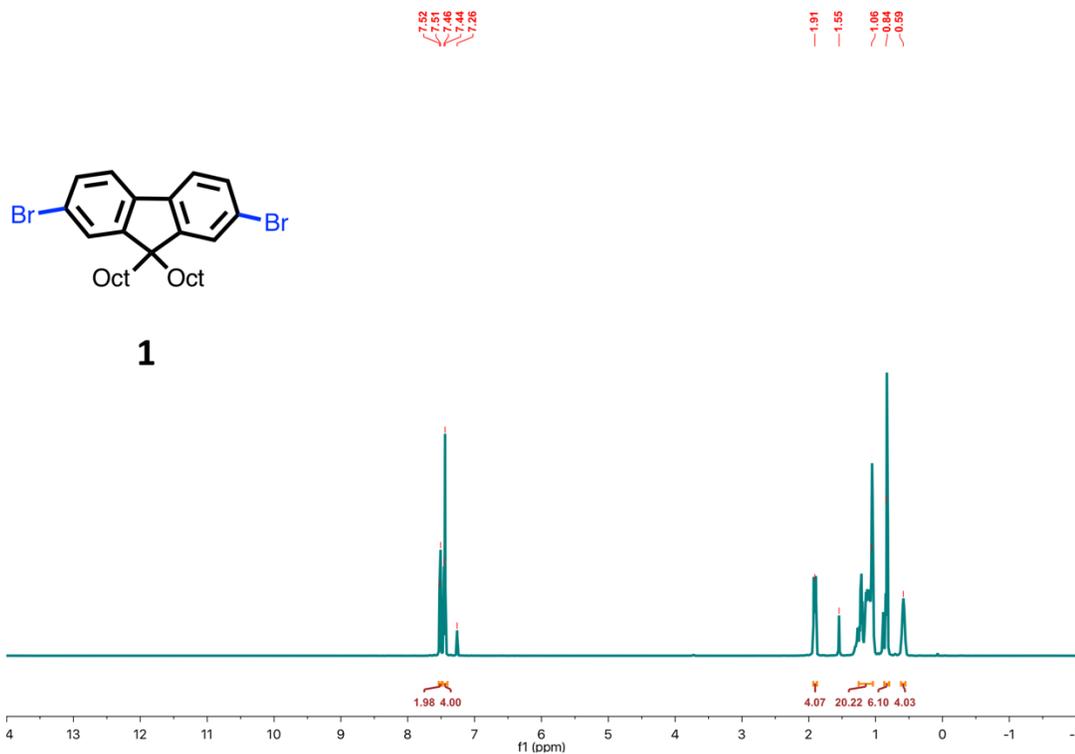


Figure S1. ¹H NMR of 9,9-bis(octyl)-2,7-dibromofluorene (**1**). Collected in CDCl₃ at 25 °C and 500 MHz. Referenced to previous reports.³

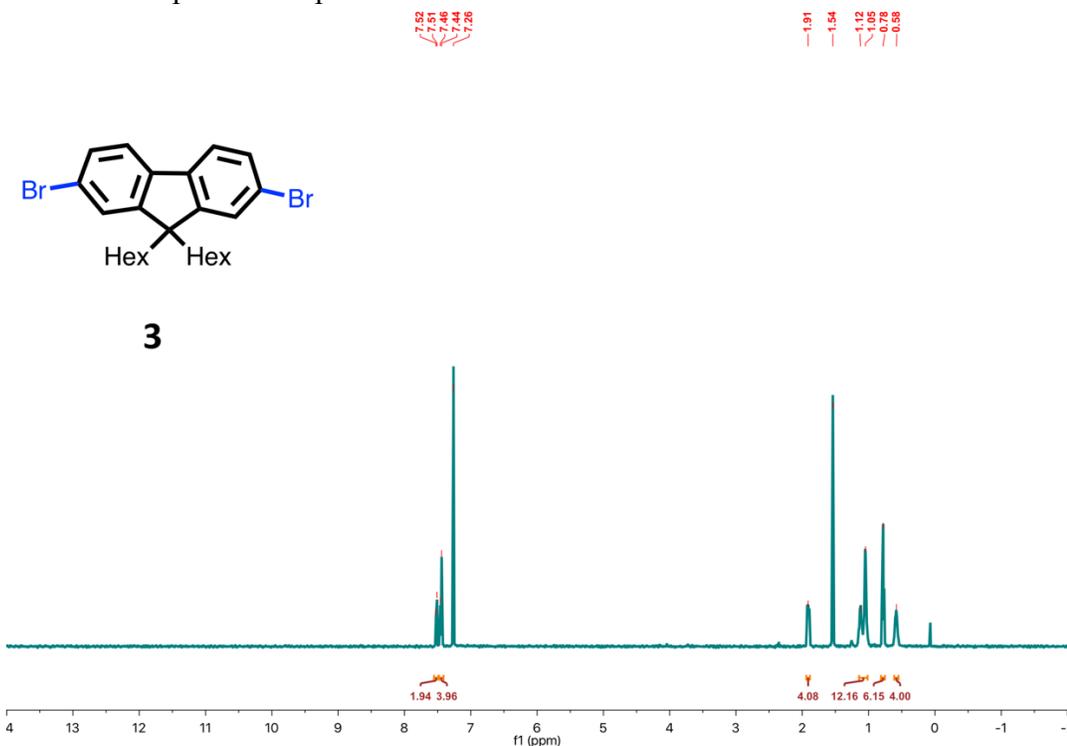


Figure S2. ¹H NMR of 9,9-bis(hexyl)-2,7-dibromofluorene (**3**). Collected in CDCl₃ at 25 °C and 500 MHz. Referenced to previous reports.⁴

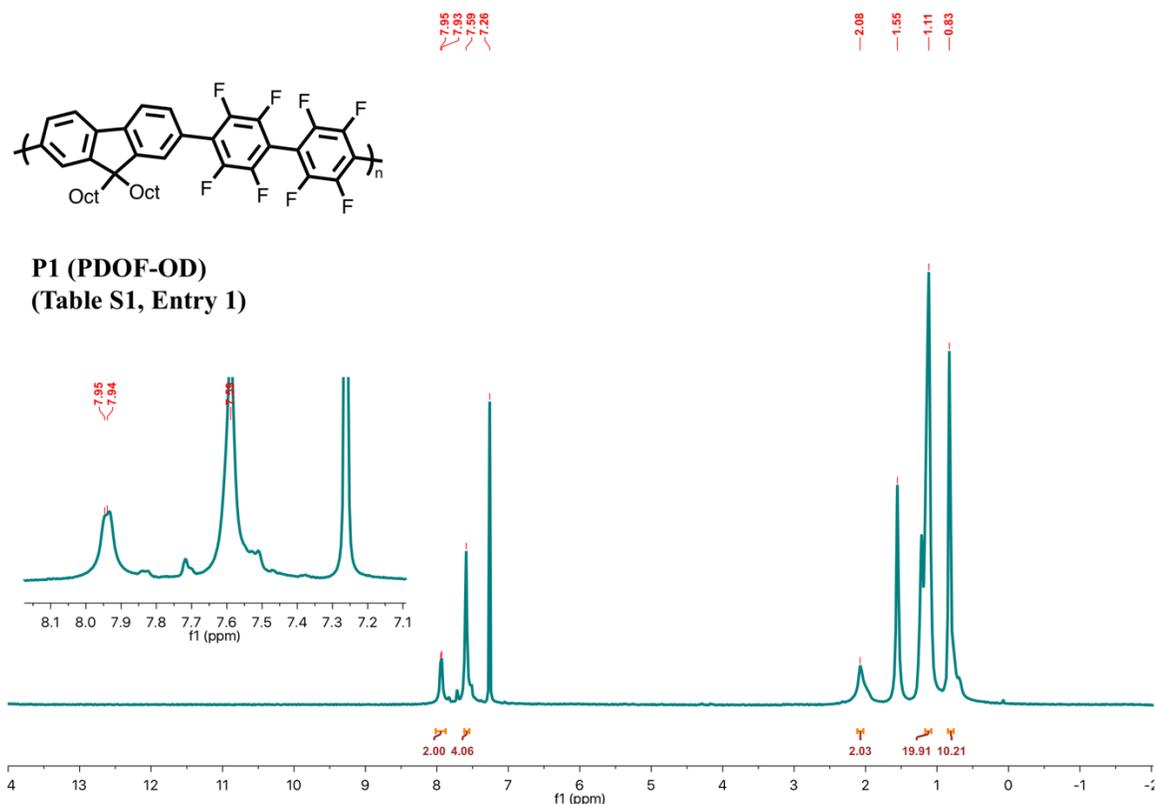


Figure S5. ^1H NMR of P1 (PDOF-OD) synthesized using the conditions in Table S1 (Entry 1). Collected in CDCl_3 at 25 °C and 500 MHz. Referenced to previous reports.⁶

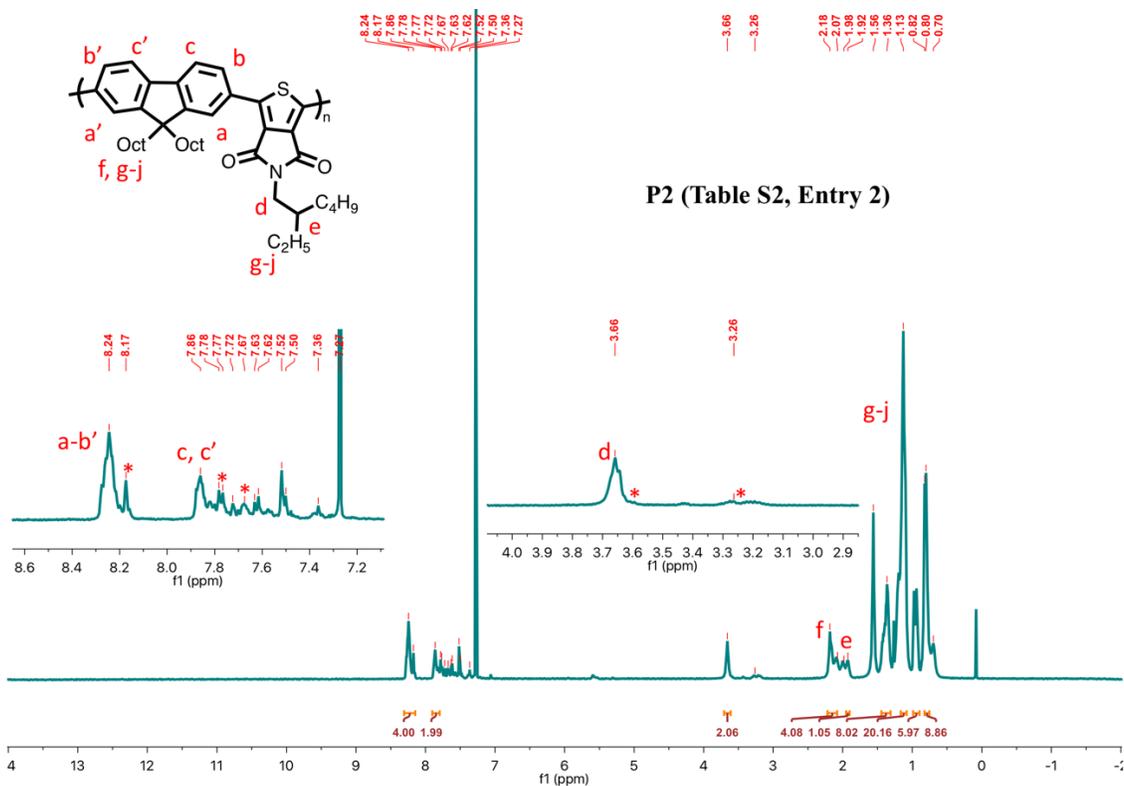


Figure S6. ^1H NMR (500 MHz) of P2 (Table S2, Entry 2) in CDCl_3 at 25 °C. End groups denoted with *.

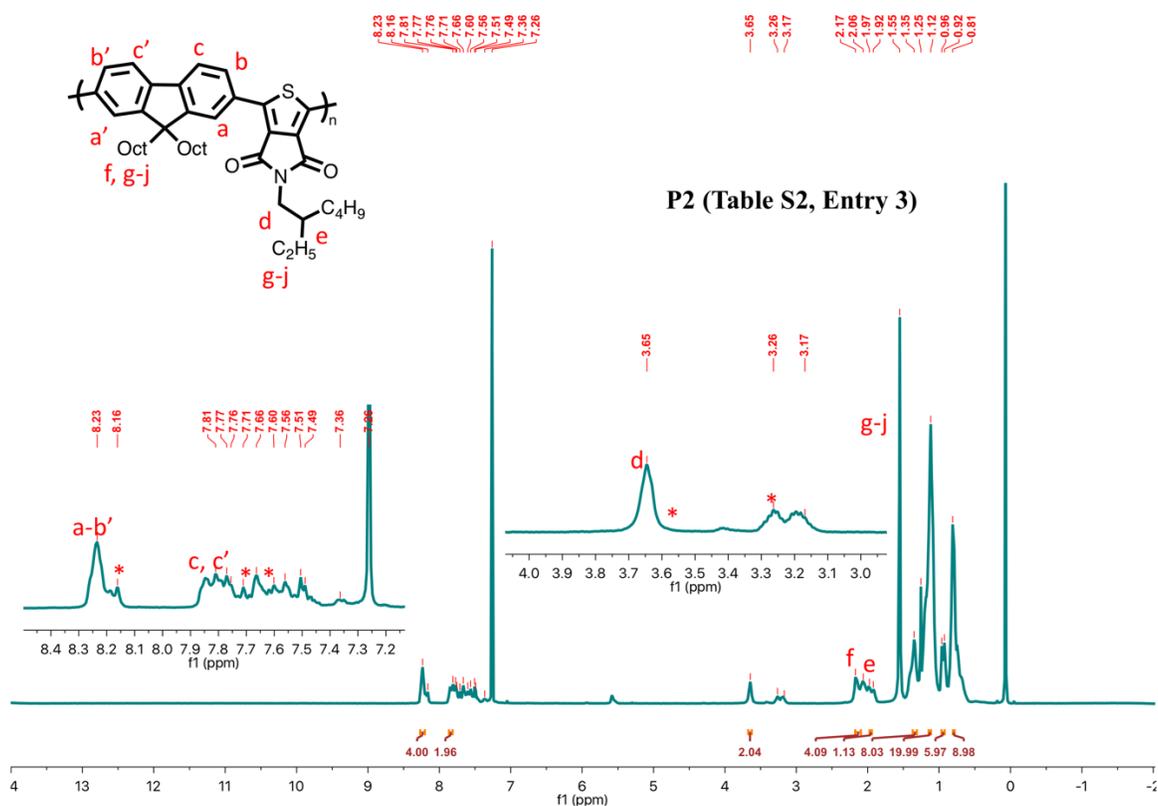


Figure S7. ¹H NMR (500 MHz) of P2 (Table S2, Entry 3) in CDCl₃ at 25 °C. End groups denoted with *.

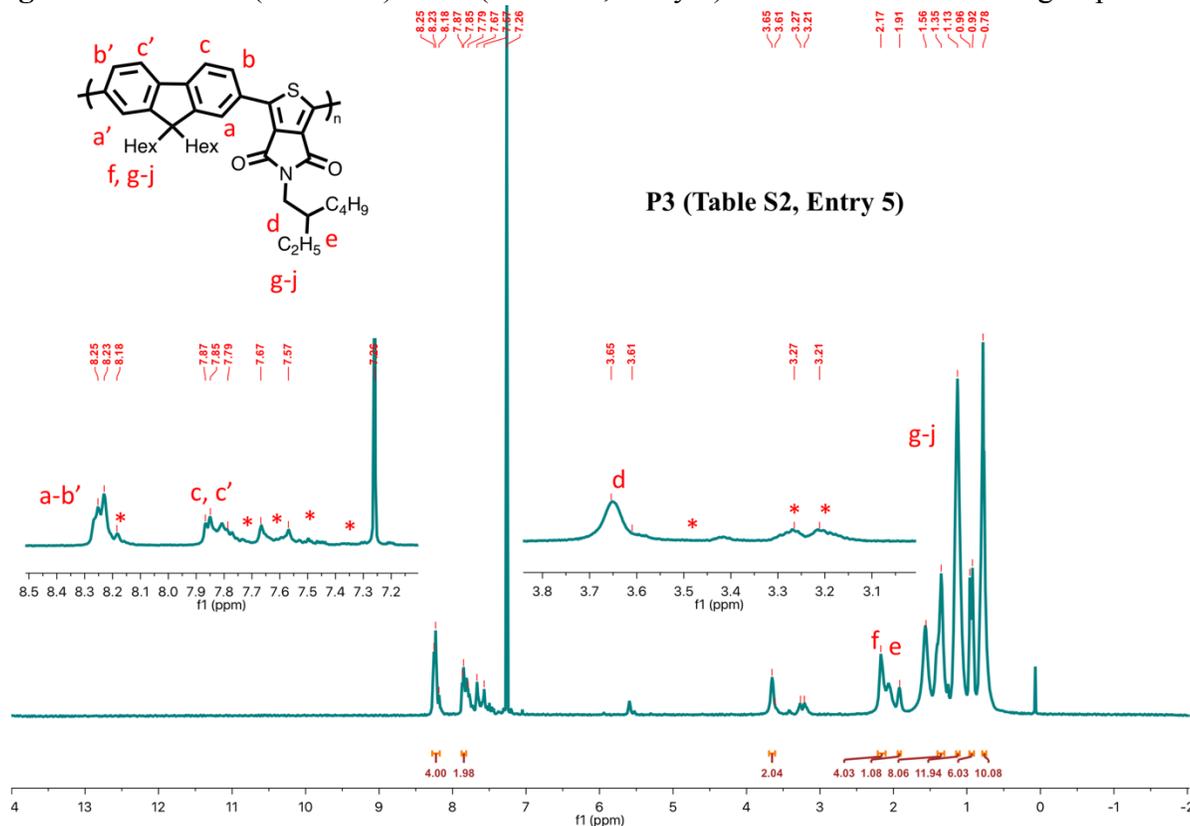


Figure S8. ¹H NMR (500 MHz) of P3 (Table S2, Entry 5) in CDCl₃ at 25 °C. End groups denoted with *.

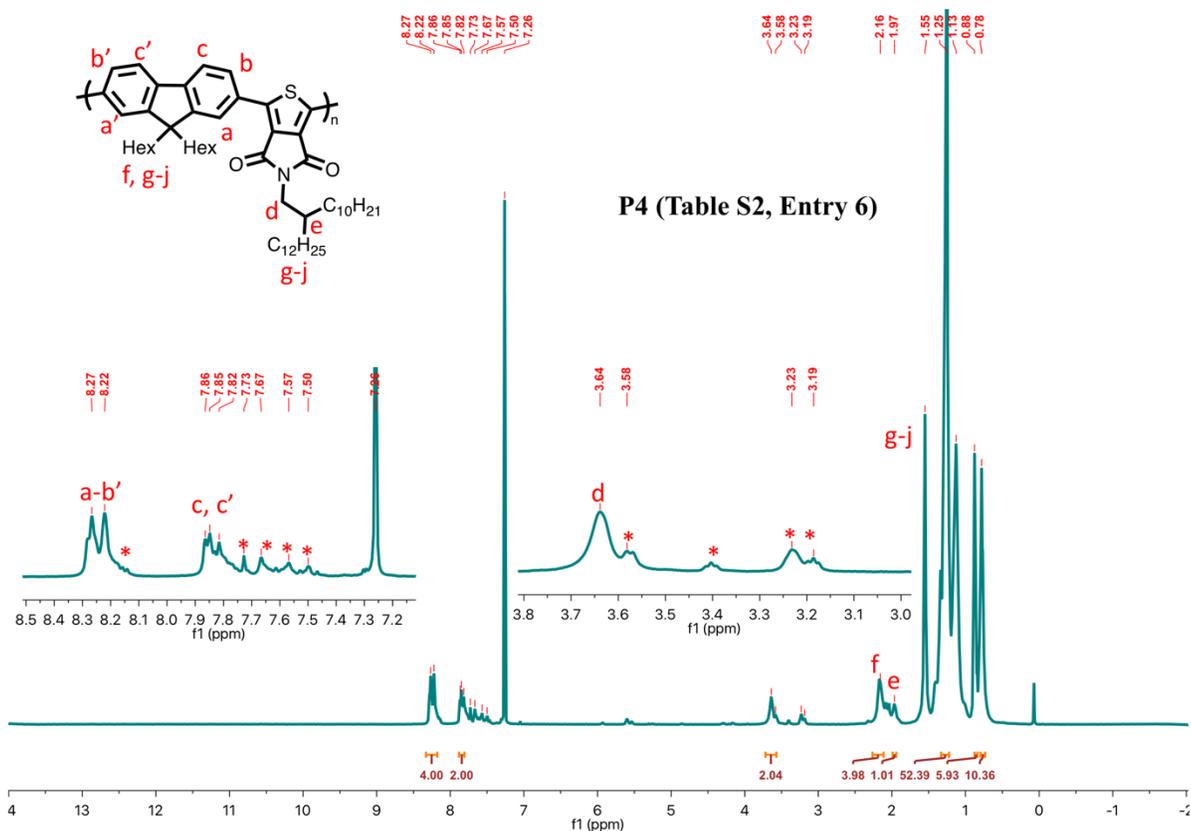


Figure S9. ¹HNMR (500 MHz) of P4 (Table S2, Entry 6) in CDCl₃ at 25 °C. End groups denoted with *.

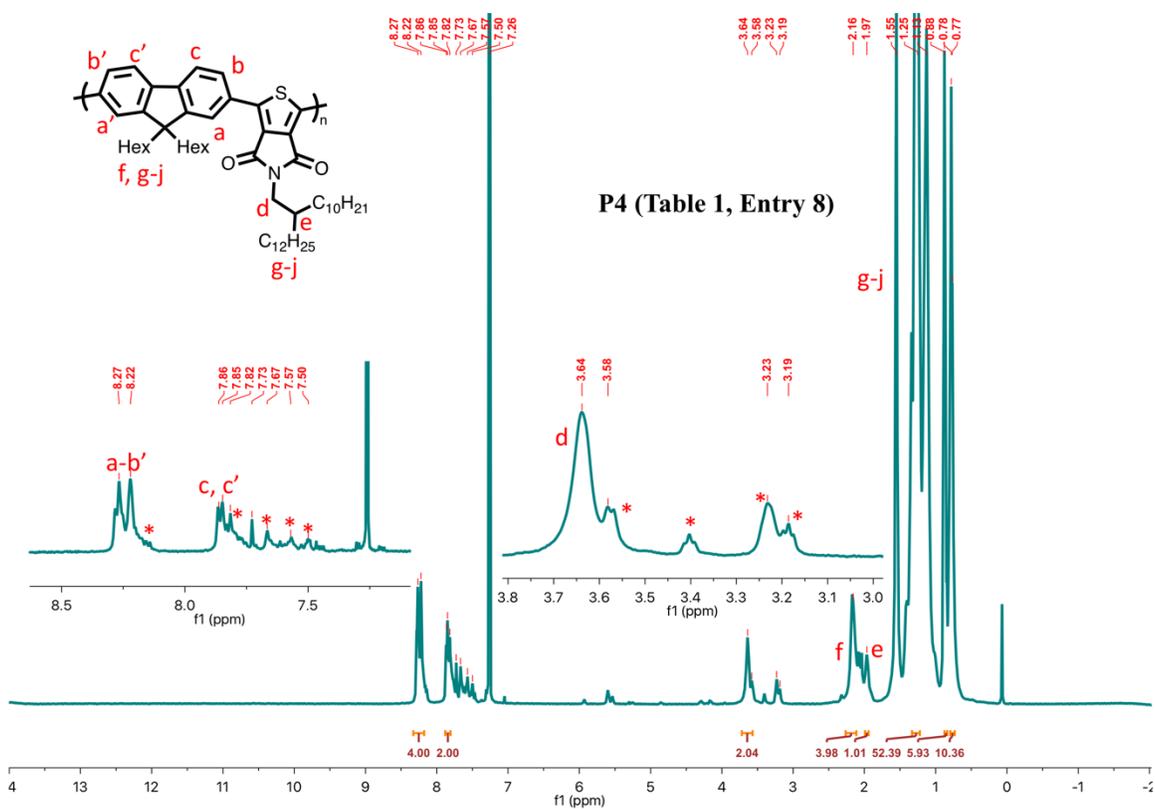


Figure S10. ¹HNMR (500 MHz) of P4 (Table 1, Entry 8) in CDCl₃ at 25 °C. End groups denoted with *.

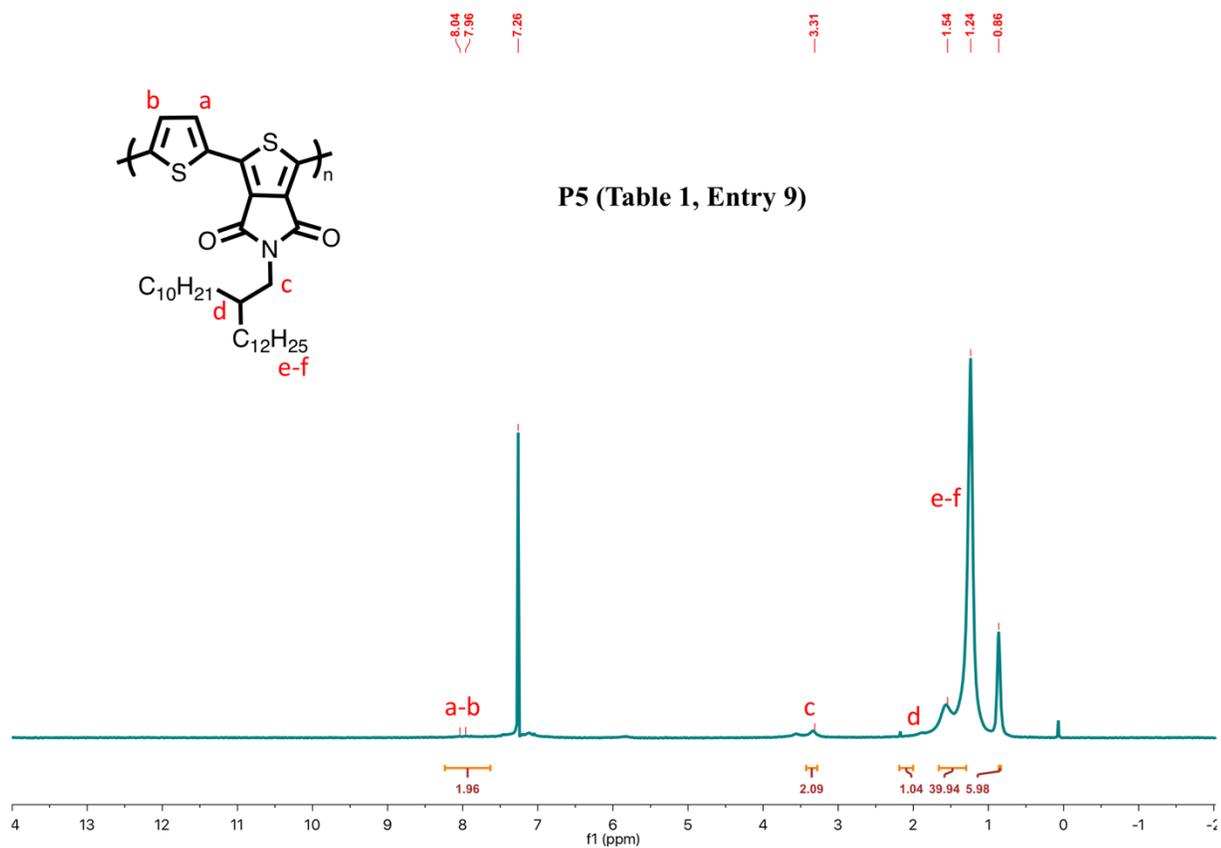


Figure S11. ¹HNMR (500 MHz) of P5 (Table 1, Entry 9) in CDCl₃ at 25 °C. End groups denoted with *.

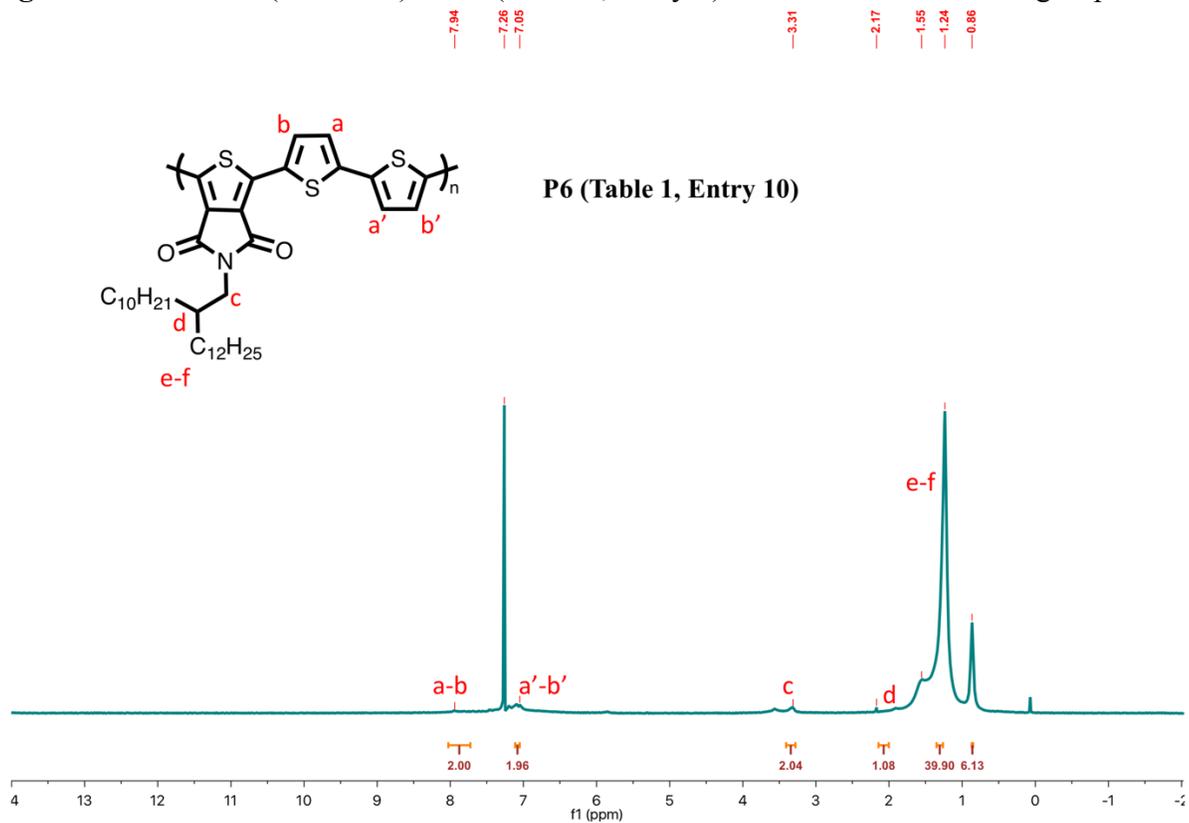
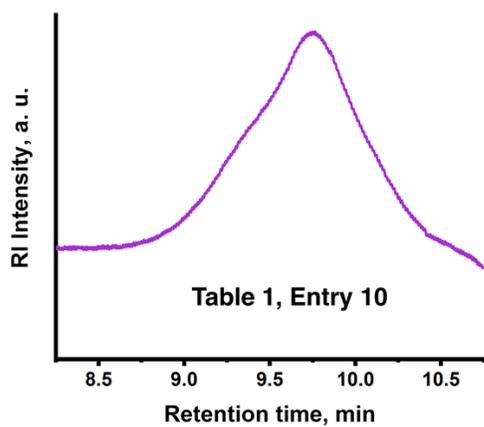
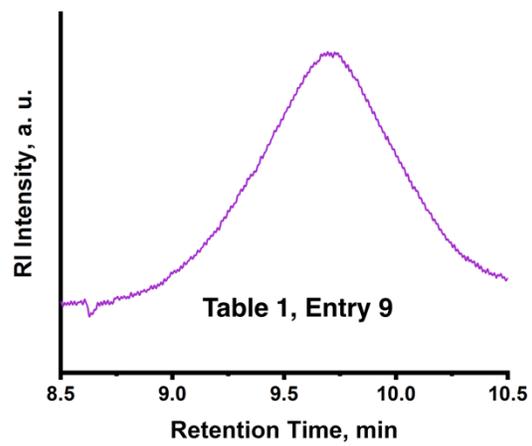
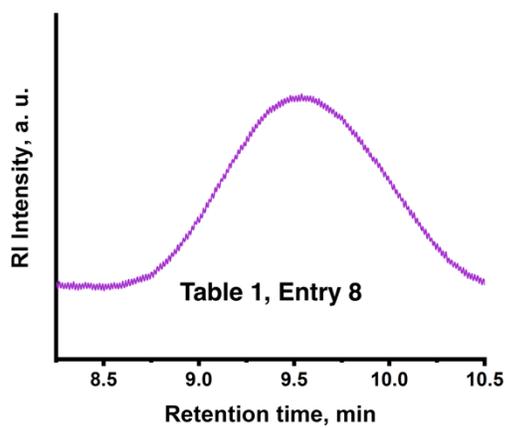
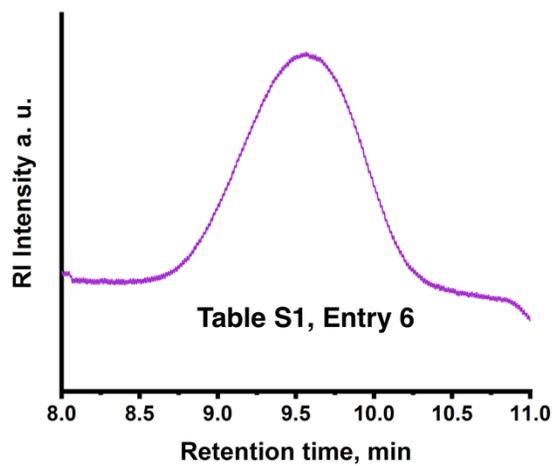
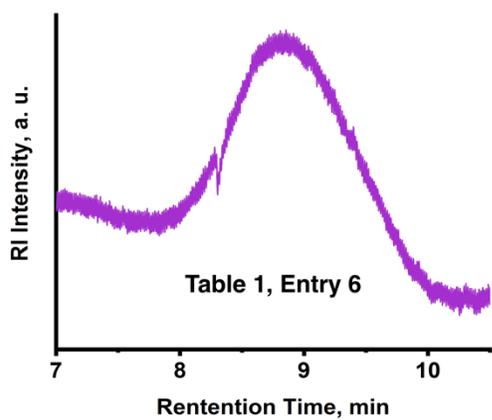


Figure S12. ¹HNMR (500 MHz) of P6 (Table 1, Entry 10) in CDCl₃ at 25 °C. End groups denoted with *.

7. GPC Traces



8. References

- (1) Pankow, R. M.; Ye, L.; Thompson, B. C. Copper Catalyzed Synthesis of Conjugated Copolymers Using Direct Arylation Polymerization. *Polym. Chem.* **2018**, *9* (30), 4120–4124.
- (2) Pankow, R. M.; Ye, L.; Thompson, B. C. Influence of an Ester Directing-Group on Defect Formation in the Synthesis of Conjugated Polymers via Direct Arylation Polymerization (DAP) Using Sustainable Solvents. *Polym. Chem.* **2019**, *10* (33), 4561–4572.
- (3) Peng, F.; Zhong, Z.; Ma, Y.; Huang, Z.; Ying, L.; Xiong, J.; Wang, S.; Li, X.; Peng, J.; Cao, Y. Achieving Highly Efficient Blue Light-Emitting Polymers by Incorporating a Styrylarylene Amine Unit. *J. Mater. Chem. C* **2018**, *6* (45), 12355–12363. <https://doi.org/10.1039/C8TC04411B>.
- (4) Voortman, T. P.; Chiechi, R. C. Thin Films Formed from Conjugated Polymers with Ionic, Water-Soluble Backbones. *ACS Appl. Mater. Interfaces* **2015**, *7* (51), 28006–28012.
- (5) Ozdemir, M.; Choi, D.; Kwon, G.; Zorlu, Y.; Cosut, B.; Kim, H.; Facchetti, A.; Kim, C.; Usta, H. Solution-Processable BODIPY-Based Small Molecules for Semiconducting Microfibers in Organic Thin-Film Transistors. *ACS Appl. Mater. Interfaces* **2016**, *8* (22), 14077–14087.
- (6) Pankow, R. M.; Ye, L.; Thompson, B. C. Sustainable Synthesis of a Fluorinated Arylene Conjugated Polymer via Cu-Catalyzed Direct Arylation Polymerization (DAP). *ACS Macro Lett.* **2018**, *7* (10), 1232–1236.