Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Copper Catalyzed Synthesis of Conjugated Copolymers using Direct Arylation Polymerization

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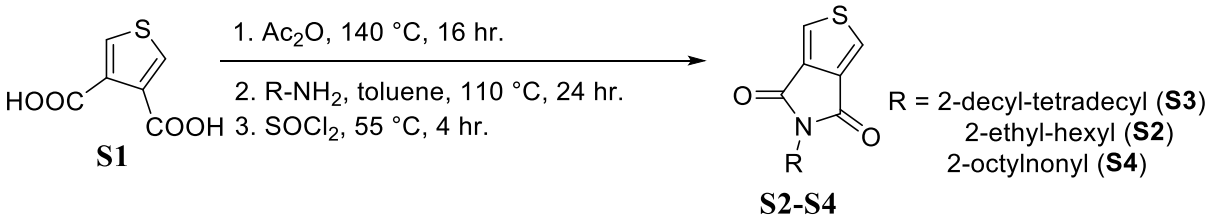
1. General

All reactions were performed under dry N_2 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. Na_2CO_3, K_2CO_3, and Cs_2CO_3 were ground into a fine powder and dried at 120 °C in a vacuum oven before use. Tetrahydrofuran (THF) was dried over sodium/benzophenone before distillation. Anhydrous N,N-dimethylacetamide (DMA) and N,N,-dimethylformamide (DMF) were used. All other solvents, such as N,N-diethylacetamide (DEA) and chlorobenzene (CB) were dried over CaH_2 and distilled onto activated molecular sieves (4 Å) prior to use. All NMR were recorded at 25 °C using $CDCl_3$ on either a Varian Mercury 400 MHz, Varian VNMRS-500 MHz, or a Varian VNMR-600 MHz. All spectra were referenced to $CHCl_3$ (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 65 °C until dissolved, cooled to room temperature, and filtered through a 0.2 μm PTFE filter.

2. Monomer Syntheses



General procedure for 5-Alkyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione Syntheses.

A 250 mL single neck round-bottom flask with a stir-bar was charged with **S1** (5 g, 29.04 mmol) and Ac_2O (100 mL). A condenser was attached and the mixture heated to 140 °C for 16 hr under N_2. After cooling, the condenser was removed and the excess Ac_2O was vacuum distilled off. To the same flask, the alkylamine (1.5 equiv.) and toluene (120 mL) were added, the condenser reattached, and the mixture heated at 110 °C for 24 hour under N_2. The mixture was cooled and the volatiles stripped via rotary evaporation. $SOCl_2$ (42 g, 356 mmol, 26 mL) was then added to the flask, the condenser reattached, and it was heated at 55 °C for 4 hr. After cooling, the mixture was added slowly to stirring ice water (200 mL) via pipette and it was then neutralized with $NaHCO_3$. The solid was filtered off, collected, chromatographed (1:1 DCM/hexanes) and recrystallized with EtOH to afford a white solid.

*5-(2-ethylhexyl)-4*H-*Thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (S2).*

Yield: 62%.^{1}H NMR 500 MHz ($CDCl_3$): δ (ppm) 7.80 (s 2H), 3.52 (d, J = 7.5 Hz, 2H), 1.83-1.78 (m, 1H), 1.36-1.26 (m, 8H), 0.92-0.87 (m, 6H). ^{13}C NMR ($CDCl_3$): δ (ppm) 162.9, 136.6, 125.4, 42.4, 38.2, 30.5, 28.5, 23.8, 23.0, 14.1, 10.4. Consistent with reported values.[1]

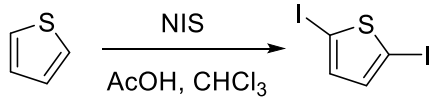
*5-(2-decyltetradecyl)-4*H-*Thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (**S3**).*

Yield: 83%.^{1}H NMR 500 MHz ($CDCl_3$): δ (ppm) 7.80 (s 2H), 3.50 (d, J = 7.0 Hz, 2H), 1.89-1.80 (m, 1H), 1.34-1.24 (m, 40H), 0.88 (t, 6H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$): δ (ppm) 162.9,

136.6, 125.4, 42.8, 36.9, 31.4, 30.0, 29.7-29.3 (overlap), 26.3, 22.7, 14.1. Consistent with reported values.[2]

*5-(2-octylnonyl)-4*H*-Thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (**S4**).*

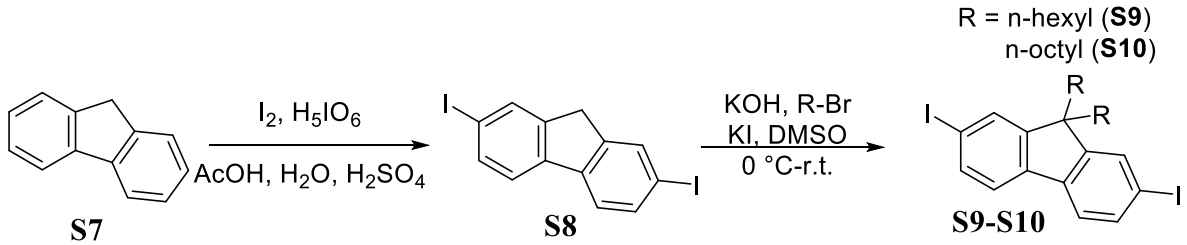
Yield: 90%.^{1}H NMR 500 MHz ($CDCl_3$): δ (ppm) 7.77 (s 2H), 4.13-4.07 (m, 1H), 2.06-2.00 (m, 2H), 1.69-1.62 (m, 2H), 1.27-1.22 (m, 24H), 0.85 (t, 6H, J = 6.0 Hz). ^{13}C NMR ($CDCl_3$): δ (ppm) 163.0, 136.5, 125.2, 52.73, 32.3, 31.8, 29.4, 29.3, 29.2, 26.7, 22.6, 14.1. Consistent with reported values.[3]



S5 **S6**

*2,5-Diiodothiophene (**S6**).*

In a round-bottomed flask equipped with a stir-bar NIS (2.2 g, 26.18 mmol) and **S5** (1.00 g, 11.9 mmol) were dissolved in AcOH (6 mL) and $CHCl_3$ (8 mL). The flask was shielded from light using aluminium foil, and the reaction mixture was allowed to stir overnight at room-temperature. H_2O (50 mL) was then added and the micture was extracted with $CHCl_3$ (3x25 mL). The organic layer was washed with aqueous $NaHCO_3$, brine, and then dried with $MgSO_4$. The crude was sent through a short silica-plug ($CHCl_3$) and then vacuum distilled to afford a yellow oil that slowly crystallized into a white solid (850 mg, 21%). ^{1}H NMR 500 MHz ($CDCl_3$): δ 6.94 (s, 2H) ^{13}C NMR ($CDCl_3$): δ (ppm) 138.8. 76.2. Consistent with reported values.[4,5]



S7 **S8** **S9-S10**

*2,7-Diiodofluorene (**S8**)*.

To a 3-neck round-bottomed flask equipped with a stir-bar and a condenser was added **S6** (3.2 g, 19.25 mmol), H_2O (10.4 mL), AcOH (51 mL), and H_2SO_4 (1.6 mL). It was heated at 95 °C until **S6** dissolved. Then the temperature was reduced to 80 °C and I_2 (3.2 g, 12.7 mmol) and H_5IO_6 (1.4 g, 6.35 mmol) were added. It was stirred at 80 °C until the disappearance of I_2 was observed (approximately 2 hours) and then cooled to room temperature. The reaction mixture was then poured into water (200 mL), $NaHSO_3$ aq. was added to quench trace I_2, and $NaHCO_3$ was added to quench excess acid. The solid was then filtered off and collected. Recrystallized from MeOH/$CHCl_3$ to yield an off-white, fibrous solid (2.9 g, 36%). ^{1}H NMR 400 MHz ($CDCl_3$): δ (ppm) 7.88 (s, 2H) 7.70 (d, 2H, J = 8.0 Hz), 7.50 (d, 2H, J = 8.0 Hz). Consistent with reported values.[6]

General procedure for 9,9-Bis(alkyl)-2,7-diiodofluorene Syntheses (S9-S10).

To a 3-neck round-bottomed flask under N_2 atmosphere with DMSO (8 mL) at 0 °C was added ground KOH (9.5 mmol, 530 mg), KI (0.19 mmol, 32 mg), **S7** (1.6 mmol, 670 mg), and the alkyl bromide (2.2 equivalents). It was slowly allowed to reach room temperature by stirring overnight. H_2O was then added (10 mL) and the mixture was extracted with hexanes. 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 recrystallized using EtOH to obtain colorless crystals.

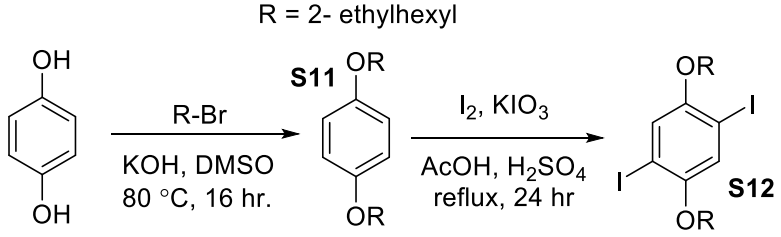
*9,9-Bis(hexyl)-2,7-diiodofluorene (**S9**).*

Yield: 29%. ^{1}H NMR 500 MHz ($CDCl_3$): δ (ppm) 7.66-7.63 (m, 4H), 7.41 (d, 2H, J = 8.0 Hz), 1.90-1.87 (m, 4H), 1.27-1.05 (m, 20H), 0.83 (t, 6H, J = 10 Hz), 0.59-0.56 (m, 4H) ^{13}C NMR

($CDCl_3$): δ (ppm) 152.5, 139.8, 136.0, 132.0, 121.5, 93.1, 55.5, 40.1, 31.8, 29.8, 29.2, 29.1, 23.6, 22.6, 14.1. Consistent with reported values.[7]

*9,9-Bis(octyl)-2,7-diiodofluorene (**S10**).*

Prepared in a similar as **S8**, but with n-octylbromide in place of n-hexylbromide. Yield: 80%. ^{1}H NMR 500 MHz ($CDCl_3$): δ (ppm) 7.66-7.64 (m, 4H), 7.41 (d, 2H, J = 7.5 Hz), 1.91-1.87 (m, 4H), 1.16-1.04 (m, 12H), 0.78 (t, 6H, J = 8.0 Hz), 0.61-0.55 (m, 4H) ^{13}C NMR ($CDCl_3$): δ (ppm) 152.5, 139.7, 136.0, 132.0, 121.5, 93.1, 55.5, 40.1, 31.4, 29.6, 23.6, 22.6, 14.0. Consistent with reported values.[8]



*1,4-bis[(2-ethylhexyloxy)]-benzene (**S11**).*

To a 3-neck 100 mL round bottom flask equipped with a stir-bar, hydroquinone (5.0 g, 45.5 mmol), KOH (10.21 g, 182 mmol), DMSO (30 mL) were added and stirred at 80 °C for 30 minutes. 2-Ethylhexyl bromide (19.22 g, 99.5 mmol) was added, and the reaction mixture was stirred overnight at 80 °C. After cooling down to room temperature, the reaction mixture was poured into 100 mL of water, extracted with diethyl ether three times, and the combined organic layers were washed with 10% NaOH solution three times. The organic layer was dried over anhydrous $MgSO_4$ followed by the removal of diethyl ether via rotary evaporation. The crude product was purified by column chromatography (hexanes:DCM = 7:3) to afford a colorless oil (9.7g, 63.8%). ^{1}H NMR 400 MHz ($CDCl_3$): δ (ppm) 7.12 (s, 2H), 3.82 (d, 4H, J = 5.0 Hz), 1.76-1.71 (m 2H), 1.53-1.27 (m, 16H), 0.94-0.89 (m, 12H). Consistent with reported values.[9]

*1,4-bis[(2-ethylhexyloxy)]-2,5-diiodobenzene (**S12**).*

To a 250 mL round bottom flask equipped with a stir-bar and a condenser, KIO_3 (1.50g, 7.02 mmol), 1,4-Bis[(2-ethylhexyl)oxy]benzene (5.89 g, 17.38 mmol), AcOH (100 mL) were added, followed by dropwise addition of H_2SO_4 (2 mL), H_2O (4 mL). I_2 (5.33g, 20.98 mmol) was added portion-wise over a period of 30 minutes, and the reaction mixture was allowed to reflux at 130 °C for 24 hours. After cooling down to room temperature, the reaction mixture was poured into 200 mL of water, quenched with $NaHSO_3$ to remove I_2, quenched with $NaHCO_3$ to remove excess acid, and extracted with diethyl ether three times. The combined organic layer was washed with saturated $NaHCO_3$ solution three times, dried over anhydrous $MgSO_4$, and concentrated under pressure. The crude product was purified by column chromatography (hexanes) to afford a colorless viscous oil (2.6g, 26.1%). ^{1}H NMR 500 MHz ($CDCl_3$): δ (ppm) 7.16 (s, 2H), 3.81 (d, J = 5.0 Hz), 1.76- 1.69 (m, 2H), 1.57-1.50 (m, 6H), 1.45-1.40 (m, 2H), 1.34-1.33 (m, 8), 0.95-0.90 (m, 12H). ^{13}C NMR ($CDCl_3$): δ (ppm) 152.9, 122.4, 86.0, 72.4, 39.5, 30.5, 29.0, 23.9, 23.0, 14.1, 11.2. Consistent with reported values.[9]

3. Polymer Syntheses

General procedure for polymerizations.

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. The aryl dihalide (0.125 mmol, 1 equiv.), the TPD acceptor (0.125 mmol, 1 equiv.), K_2CO_3 (40 equiv.), and phenanthroline (0.5 equiv) were added. The vessel was further sparged with N_2 (3 min.). Then N,N-dimethylacetamide (2.5 mL) was added and the mixture was degassed with N_2 for 15 min. CuI (0.5 equiv) was quickly added and the vessel sealed with a Teflon screw-cap. The vessel was then submerged in a pre-heated oil bath (140 °C) for 72 hours. The reaction was then cooled, and the mixture was precipitated into cold 10% NH_4OH/methanol solution, using $CHCl_3$ to dissolve any solids. The precipitate was then collected via filtration, and it was washed with water, methanol, acetone, and hexanes until the wash appeared colorless. It was then dried under high-vacuum overnight.

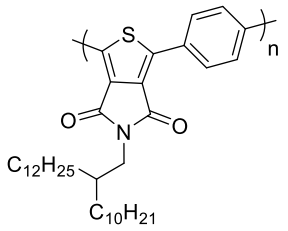
Table S1. Synthesis and optimization of P1 using Cu-catalyzed DArP.

Entry	Ligand[a]	Cat. Mol[b] %	Solvent	Temperature (°C)	Time (h)	Base	M_n (kDa)[d], Đ	Yield [d] (%)
1	phen	5	DMF/CB	140	72	Cs_2CO_3	NR	NR
2	phen	20	DMF /CB	140	72	Na_2CO_3	NR	NR
3	phen	20	DMF/CB	140	72	t-BuOLi	NP	NP
3	phen	20	DMF/CB	140	72	K_3PO_4	NR	NR
5	phen	20	DMF/CB	140	72	K_2CO_3	NP	NP
6	phen	10	THF	120	72	K_2CO_3	1.1; 1.61	34
7	phen	10	DMF	140	72	K_2CO_3	1.5, 1.77	46
8	phen	50	DMA	140	72	K_2CO_3	5.6, 2.20	23
9	phen	50	DMA	166	72	K_2CO_3	4.2, 2.85	29
10	phen	50	NMP	140	72	K_2CO_3	NR	NR
11	phen	50	DEA	140	72	K_2CO_3	5.4, 1,56	37
12	dppf	50	DMA	140	72	K_2CO_3	NR	NR
13	dmby	50	DMA	140	72	K_2CO_3	2.6, 1.68	24
14	neocup	50	DMA	140	72	K_2CO_3	NR	NR
15	phen	5	DMA	140	88	K_2CO_3	2.9, 1.62	15
16	phen	25	DMA	140	88	K_2CO_3	3.7, 2.13	49
17	phen	50	DMA	140	48	40 eq K_2CO_3	8.2, 1.64	14

[a] phenanthroline (phen), 4,4'-dimethyl-2,2'-bipyridine (dmby)1,1'-bisferrocenediyl-bis(diphenylphosphine (dppf), neocuproine (neocup). [b]99.999%-Puratrem Cu(I) iodide was used as the copper source with a 1:1 ratio to the ligand; . [c]N,N-dimethylacetamide (DMA), N-methylpyrrolidone (NMP), N,N-diethylacetamide (DEA), and chlorobenzene (CB); solvent mixtures were 3:1 cosolvent:DMF.[d]Determined for polymer products after purification; no reaction (NR), no polymer (NP).

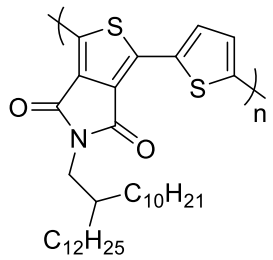
Initially, our investigation for optimal conditions for the synthesis of P1 looked at the optimal base (entries 1-5), with only K_2CO_3 providing a reaction (qualitatively) but no isolable polymer product. While t-BuOLi did provide a reaction, it was only the rapid decomposition of the monomers. At this point, we were unaware of the significance of the amide solvent and were using solvent mixtures with chlorobenzene in hopes to keep any polymer product in solution. We had observed that aryliodides only reacted, and so we were certain chlorobenzene would remain inert. Also, chlorobenzene has been proven successful in Pd-based DArP.[10] Next, through optimization of the solvent, we discovered the importance of the amide solvent (entries 6-8) with DMA providing the best M_n (5.6 kDa) along with an increase in catalyst loading (50 mol %). The importance of this solvent is further discussed in regards to Figure S2, below. We then

looked at higher temp (entry 9) and other amide solvents, such as NMP and DEA (entries 10 and 11, respectively), but the original conditions for DMA (entry 8) were still the best observed. From screening bidentate ligands (entries 12-14), only dmby (entry 13) provided polymer product albeit with lower M_n compared to phenanthroline (2.6 versus 5.6 kDa, respectively). Lowering the catalyst loading to 5 mol% (entry 15) and 25 mol% (entry 16), provided satisfactory M_n but less than that of 50 mol % (2.9 and 3.7 kDa versus 5.6 kDa). We believe the lower concentration of our conditions (0.1 M) relative to Daugulis' initial study (1 M) is a major influence in determining the need for a higher catalyst loading. Attempts to replicate Daugulis' conditions exactly, in regards to solvent (DMF), concentration (1 M), and catalyst loading (10 mol %), did not afford any polymer product, although a reaction was observed indicating the formation of very low M_n oligomers. This is likely due to the premature precipitation of the product, consequential of the low solubility in the amide solvents studied and the high concentration (1 M). Lastly, we looked at increasing the equivalents of base and found this provided the highest value for M_n (8.1 kDa).



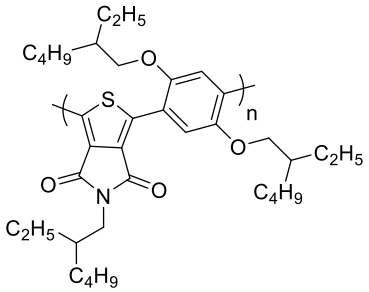
*poly[(2,5- phenylene])-alt-(5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione)] (**P1**)*.

Yellow/orange solid. ^{1}H NMR 600 MHz ($CDCl_3$): δ (ppm) 8.30-7.80 (b, 4H), 3.79-3.54 (b, 2H), 2.10-1.80 (b, 1H), 1.70-1.0 (b, 40H), 0.86 (b, 6H).



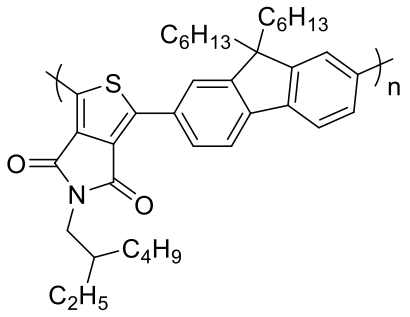
*poly[(5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione-1,3-diyl)-alt-(9,9-dihexylfluorene-2,7-diyl)] (**P2**).*

Dark purple solid. ^{1}H NMR 600 MHz ($CDCl_3$): δ (ppm) 8.03 (b, 2H), 3.56 (b, 2H), 1.91 (b, 1H), 1.25 (b, 40 H), 0.86 (b, 6H).[11]



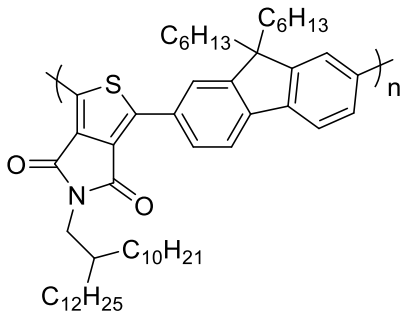
poly[(2,5-bis[(2-ethylhexyl)oxyphenylene])-alt-(5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione)] (***P3***).

Bright orange solid collected in hexanes fraction. ^{1}H NMR 600 MHz ($CDCl_3$): δ (ppm) 8.33 (b, 2H),4.18 (b, 4H), 3.59 (b, 2H), 1.94-1.85 (b, 3H), 1.57-1.15 (b, 24H), 0.94-0.83 (b, 18H).[12]



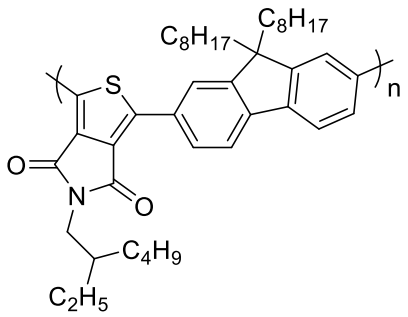
poly[(5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione-1,3-diyl)-alt-(9,9-dihexylfluorene02,7-diyl)] (***P4***).

Yellow solid. ^{1}H NMR 600 MHz ($CDCl_3$): 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).[13,14]



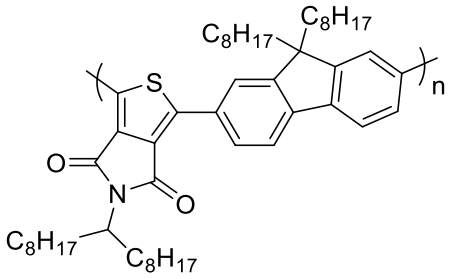
poly[(5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione-1,3-diyl)-alt-(9,9-dihexylfluorene02,7-diyl)] (***P5***).

Yellow solid. ^{1}H NMR 600 MHz ($CDCl_3$): 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).[13,14]



*poly[(5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione-1,3-diyl)-alt-(9,9-dioctylfluorene-2,7-diyl)] (**P6**).*

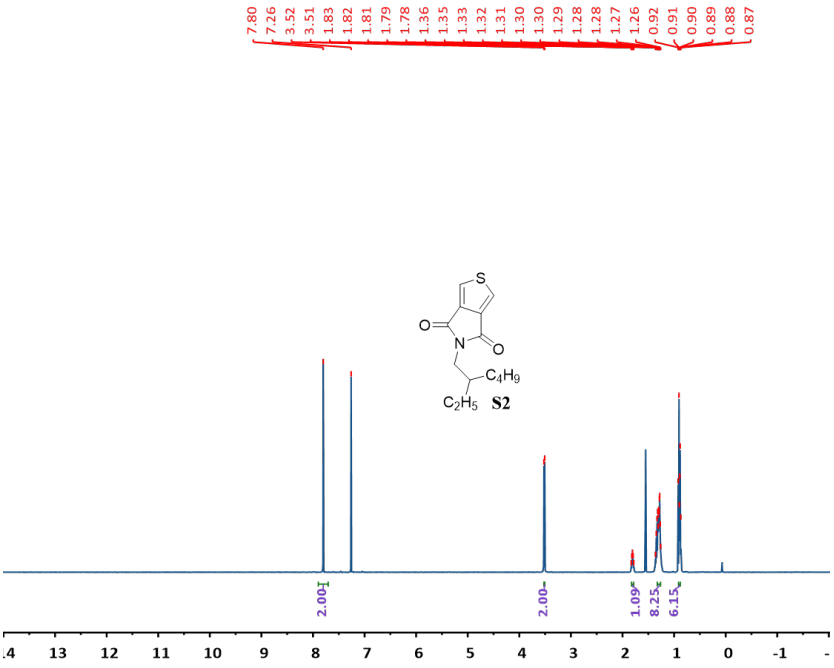
Yellow solid. ^{1}H NMR 600 MHz ($CDCl_3$): δ (ppm) 8.26-8.24 (m, 4H), 7.86 (d, 2H, J = 7.8 Hz), 3.65 (b, 2H), 2.17 (b, 4H), 1.93 (b, 1H), 1.56-1.34 (b, 8H), 1.20-1.12 (b, 20H), 0.98-0.92 (b, 6H), 0.82-0.68 (b, 10H).[13,14]



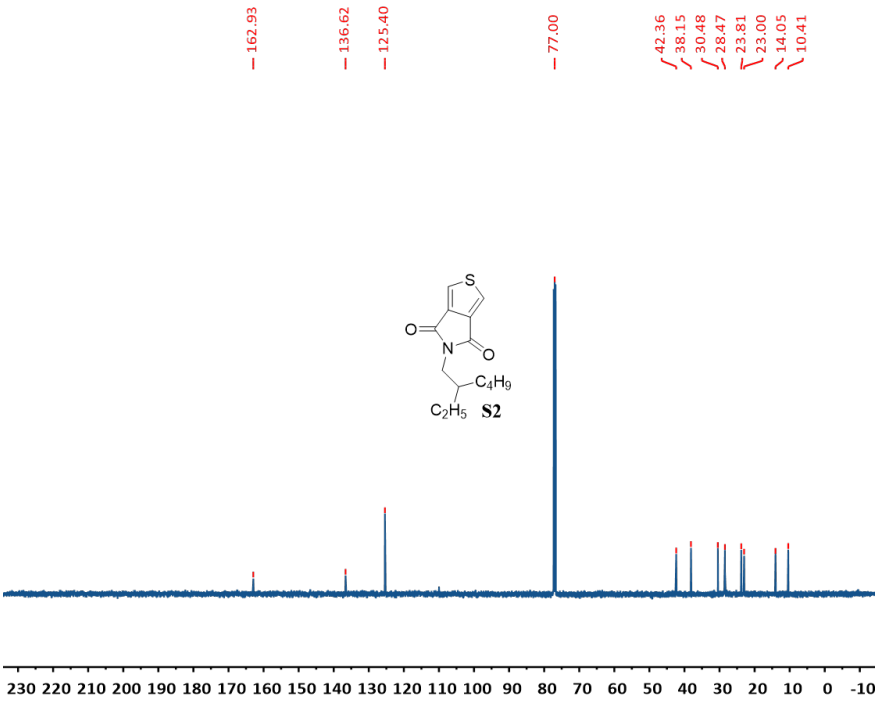
*poly[(5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione-1,3-diyl)-alt-(9,9-dioctylfluorene-2,7-diyl)] (**P7**).*

Yellow solid. ^{1}H NMR 600 MHz ($CDCl_3$): δ (ppm) 8.30 (d, 2H, J = 7.2 Hz), 8.16-8.14 (b, 2 H), 7.86 (d, 2H, J = 7.8 Hz), 4.26 (b, 1H), 2.15 (b, 6H), 1.76 (b, 2H), 1.33-1.13 (b, 44H), 0.87-0.80 (b, 16H).[13,14]

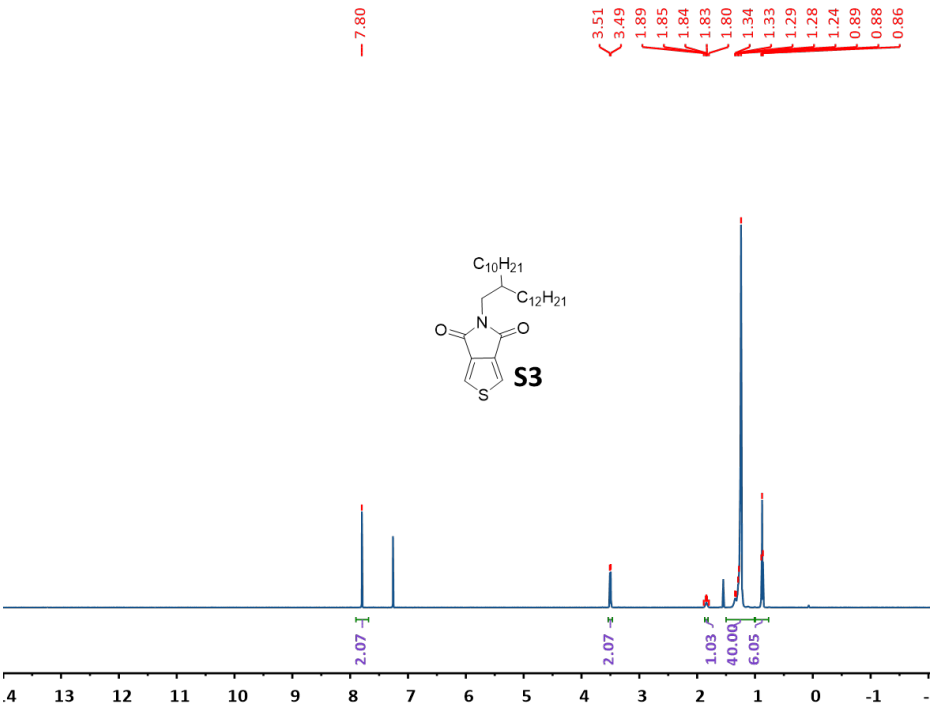
4. Monomer NMR



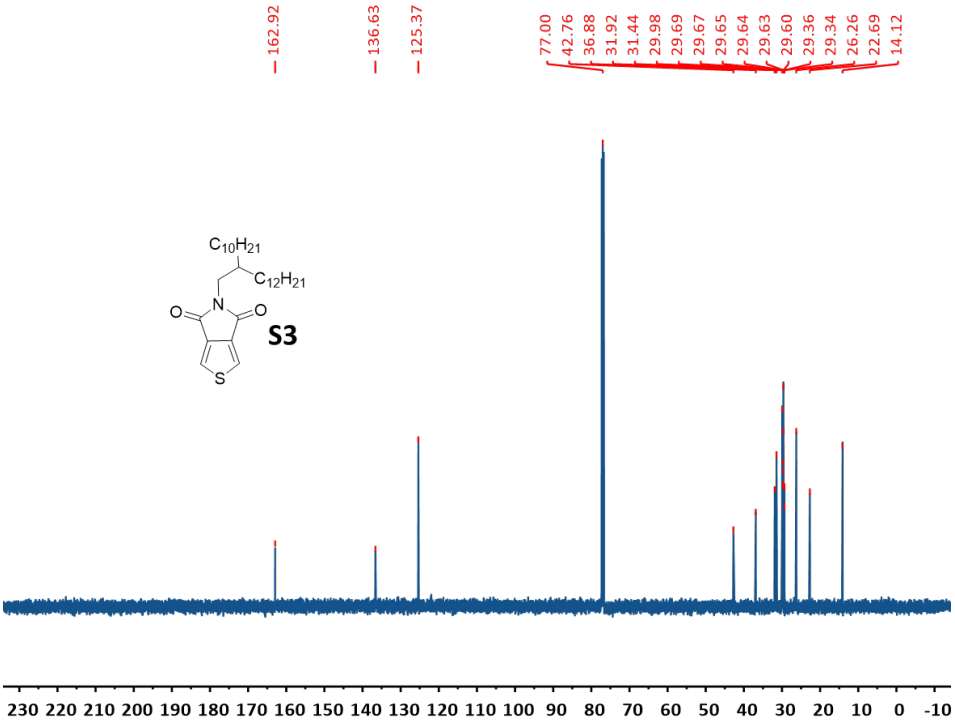
^{1}H NMR of S2 in $CDCl_3$ at 25 °C.



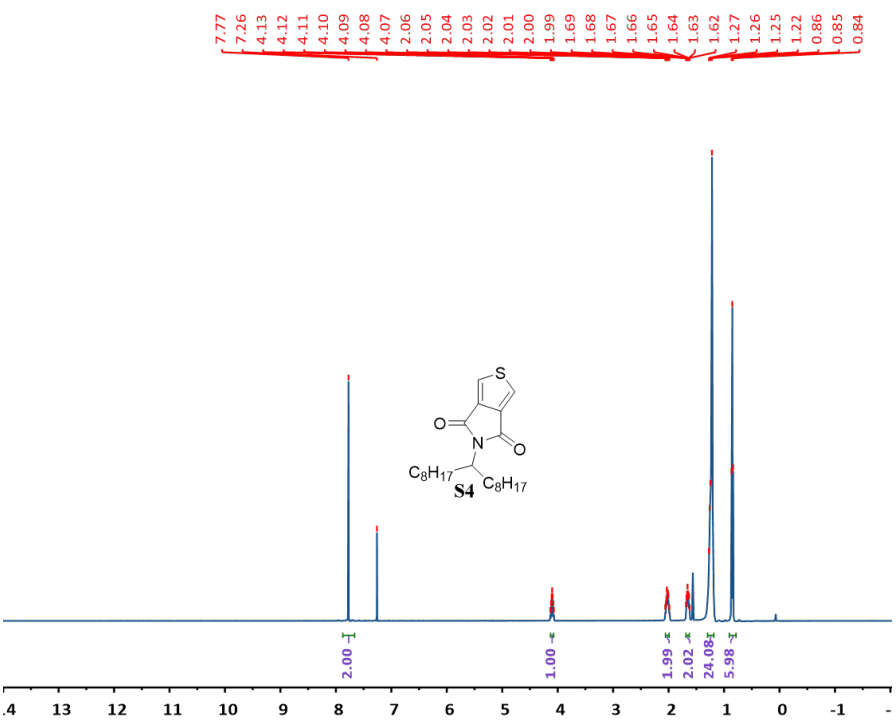
^{13}C NMR of S2 in $CDCl_3$ at 25 °C.



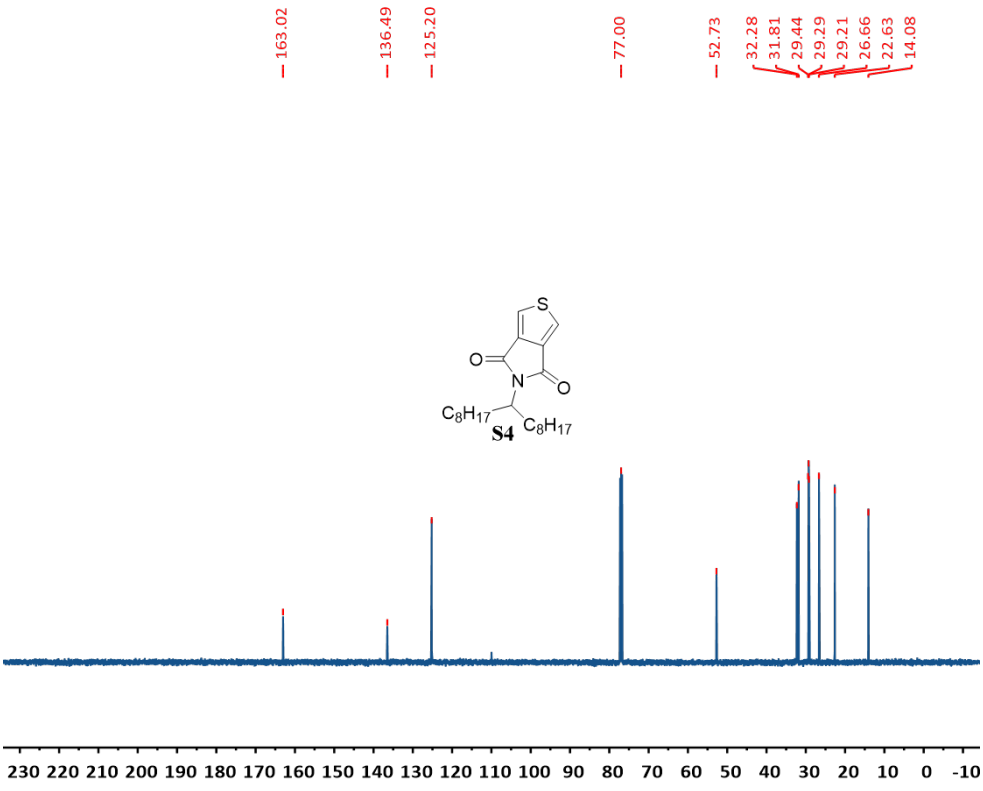
^{1}H NMR of S3 in $CDCl_3$ at 25 °C.



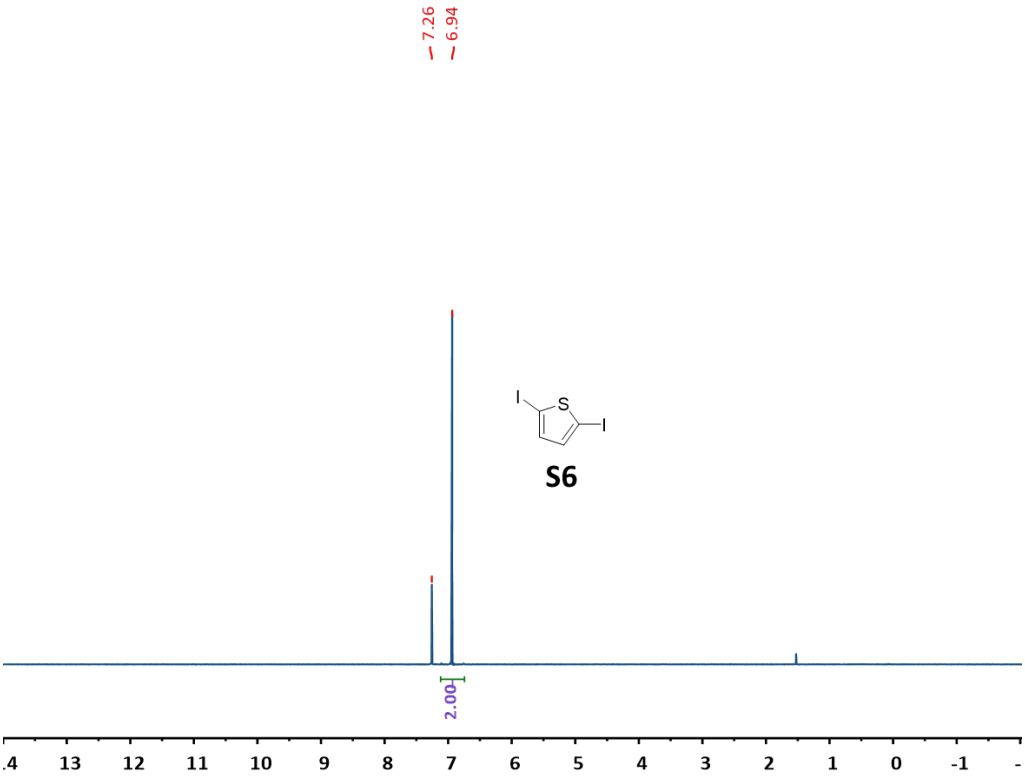
^{13}C NMR of S3 in $CDCl_3$ at 25 °C.



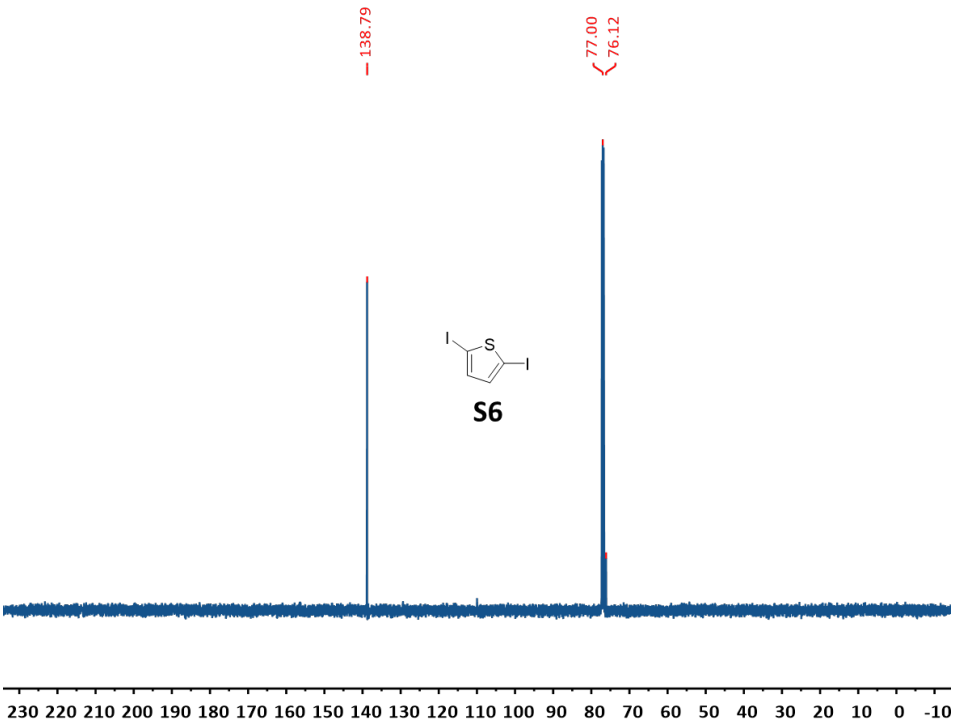
^{1}H NMR of S4 in $CDCl_3$ at 25 °C.



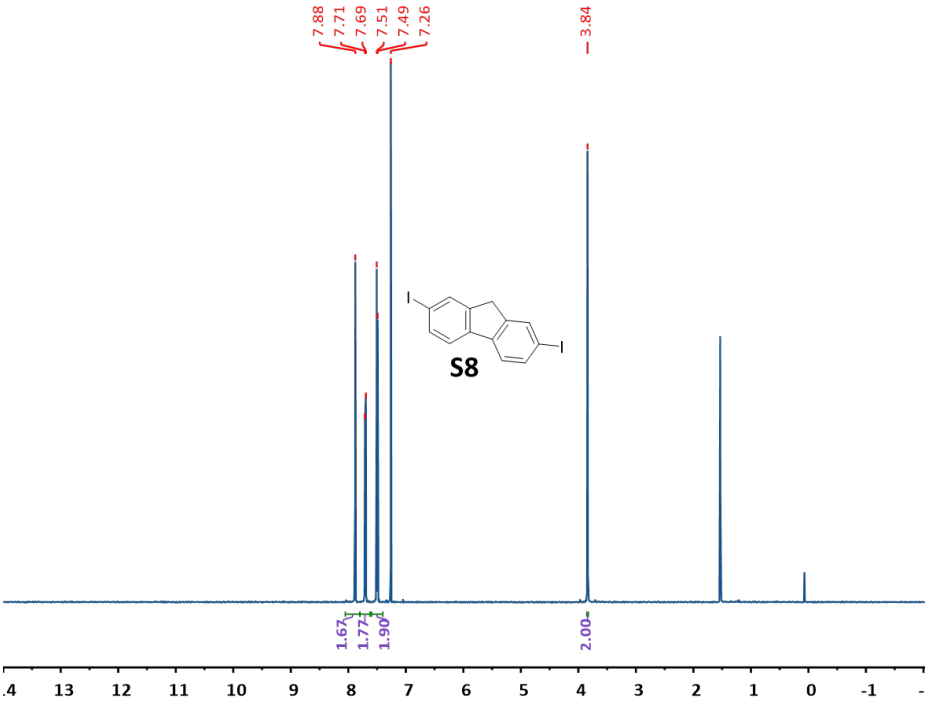
^{13}C NMR of S4 in $CDCl_3$ at 25 °C.



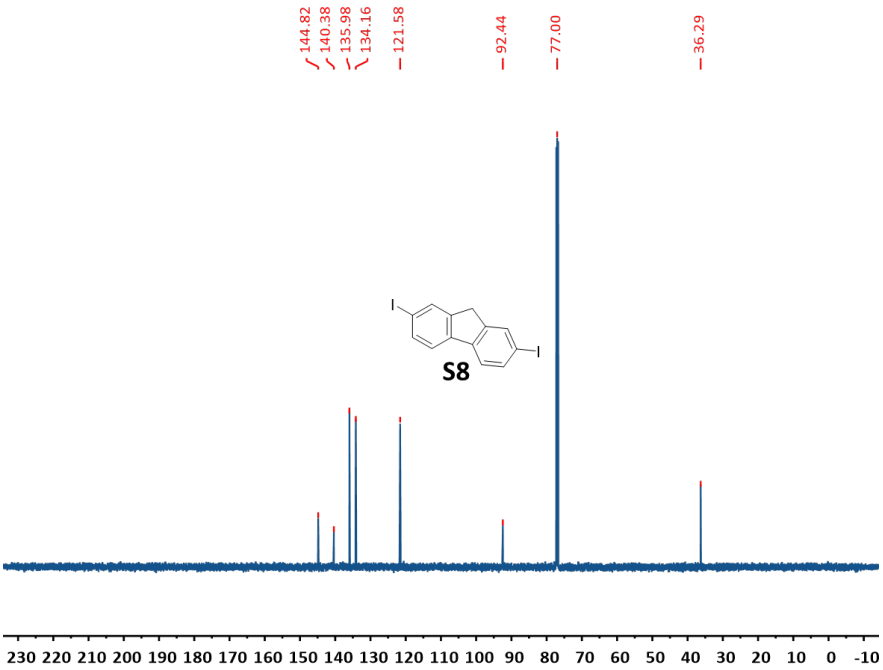
^{1}H NMR of S6 in $CDCl_3$ at 25 °C.



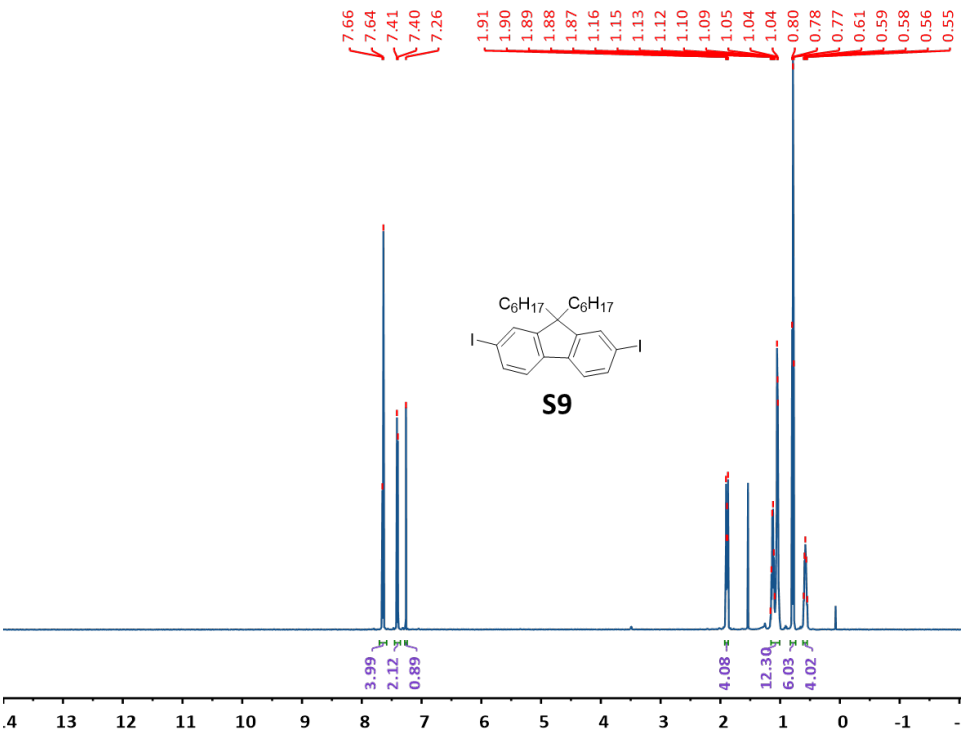
^{13}C NMR of S6 in $CDCl_3$ at 25 °C.



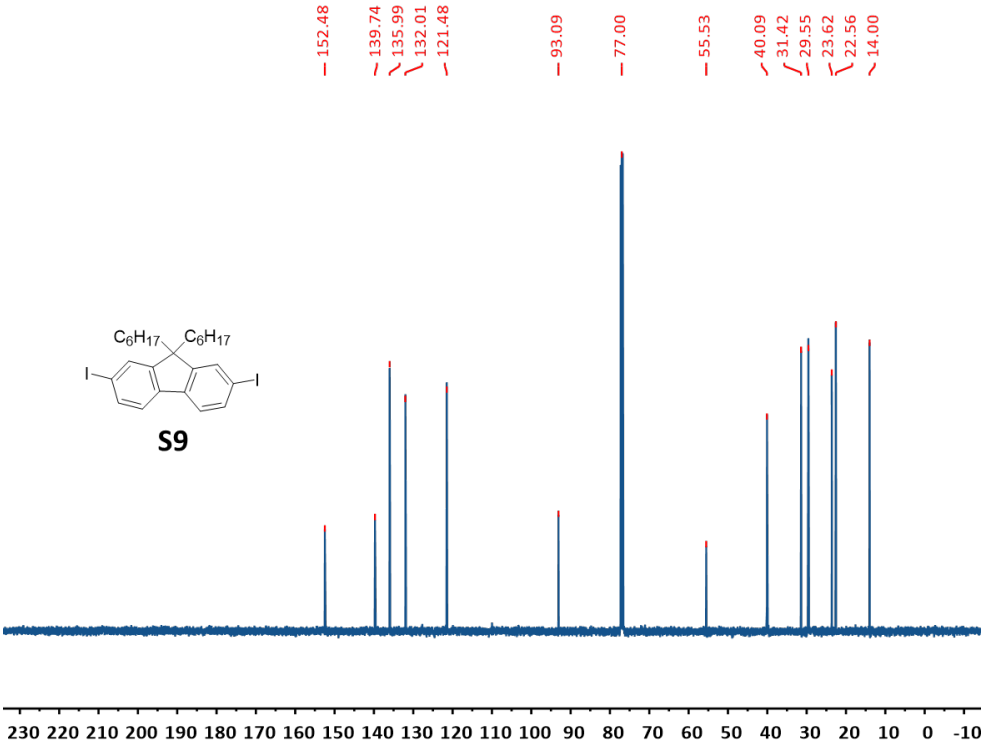
^{1}H NMR of S8 in $CDCl_3$ at 25 °C.



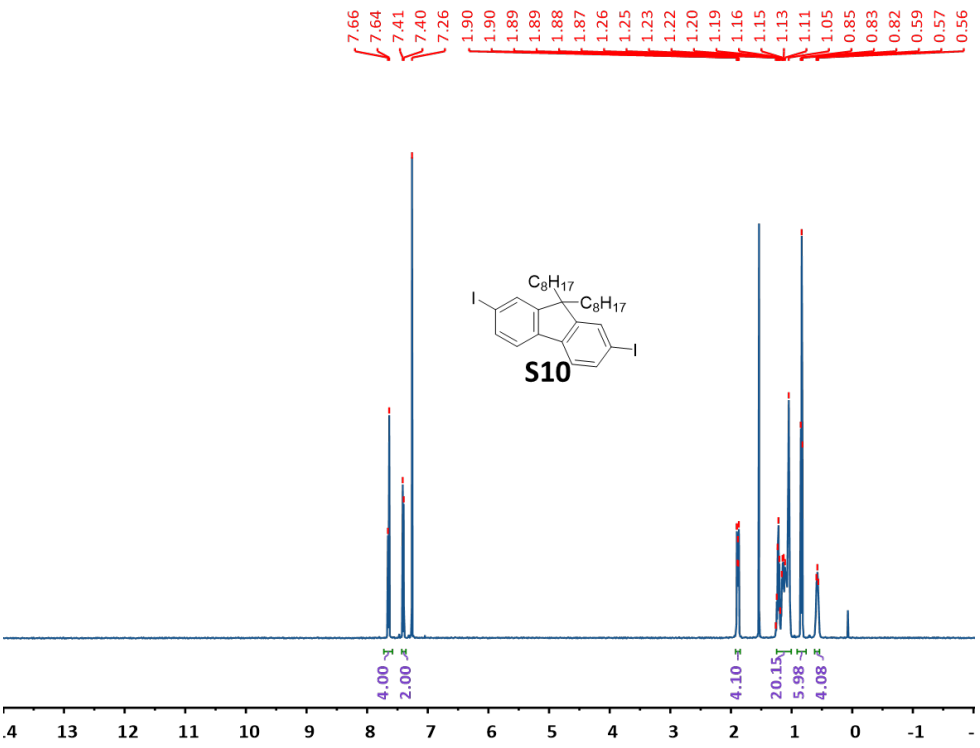
^{13}C NMR of S8 in $CDCl_3$ at 25 °C.



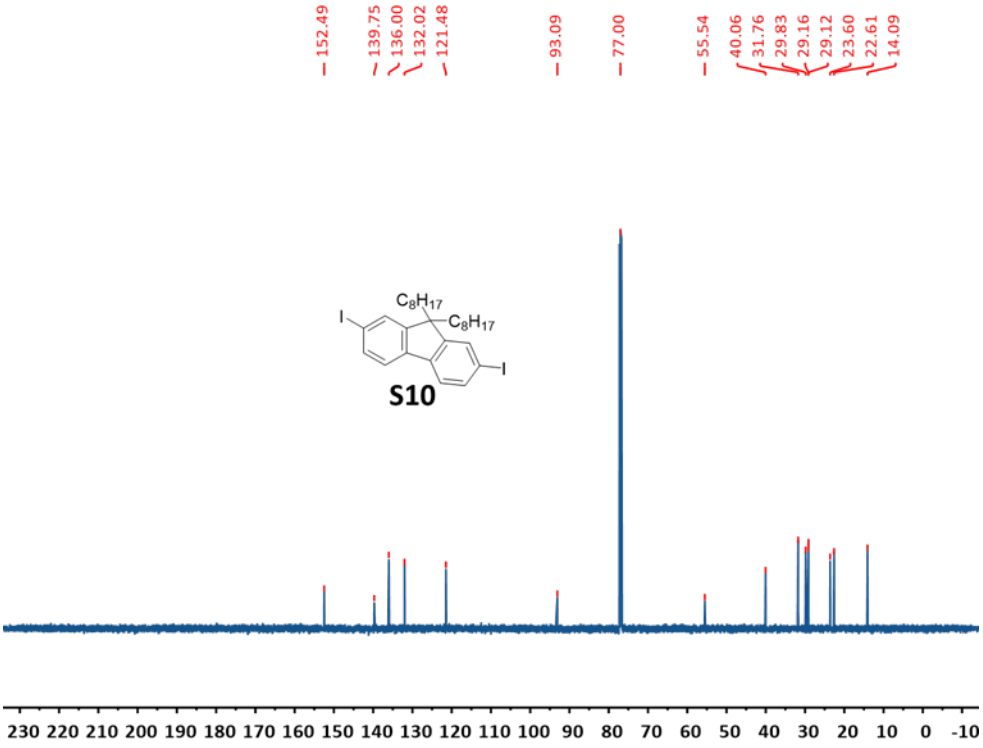
^{1}H NMR of S9 in $CDCl_3$ at 25 °C.



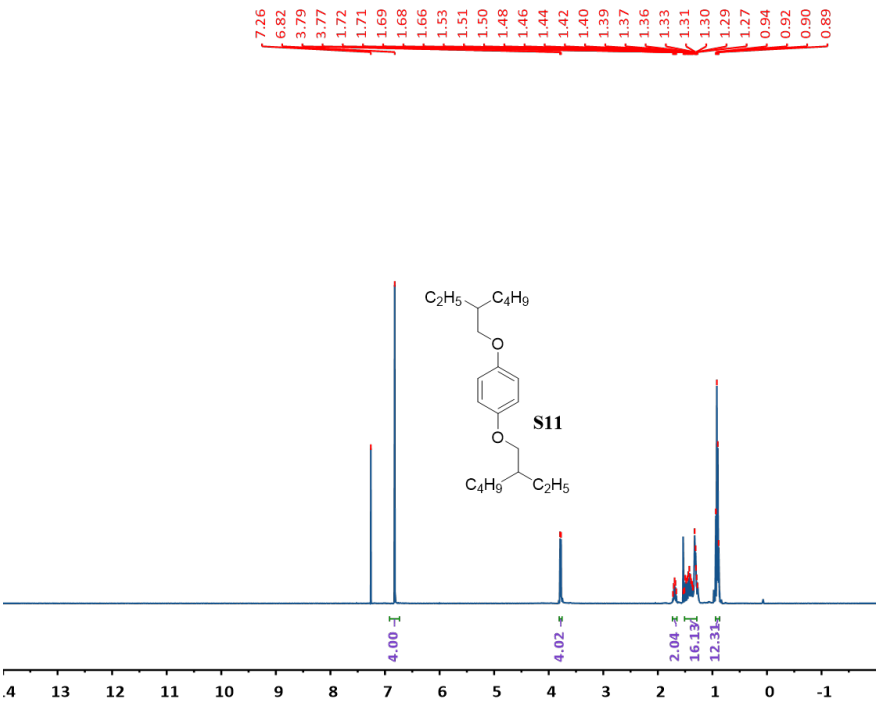
^{13}C NMR of S9 in $CDCl_3$ at 25 °C.



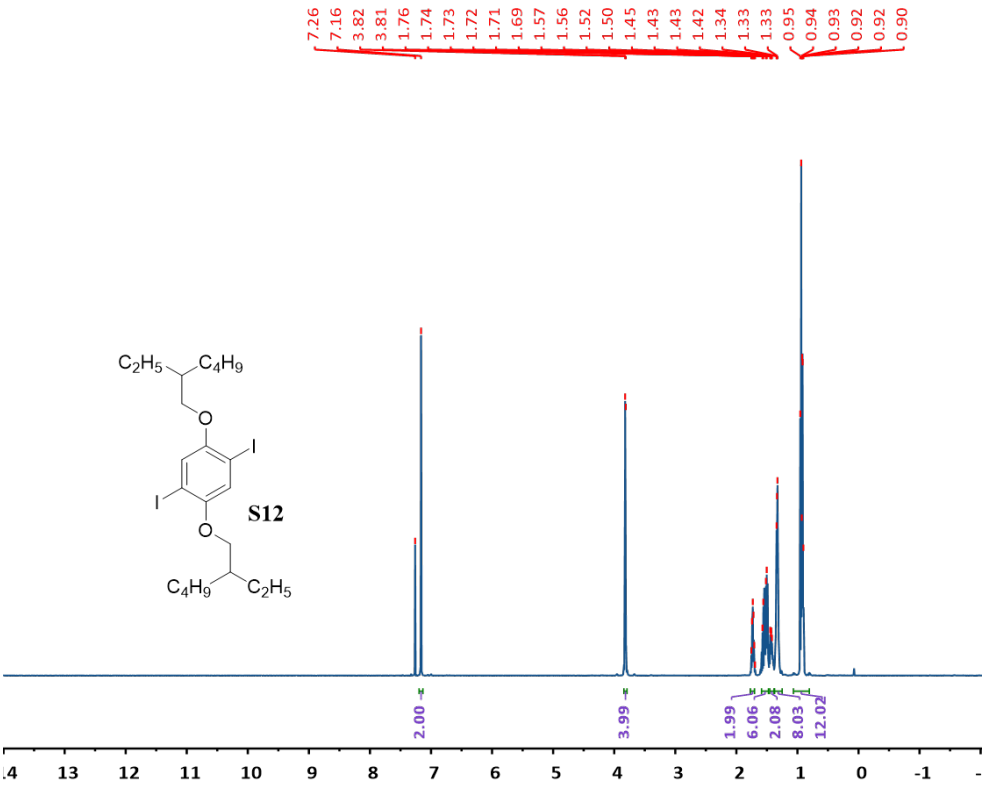
^{1}H NMR of S10 in $CDCl_3$ at 25 °C.



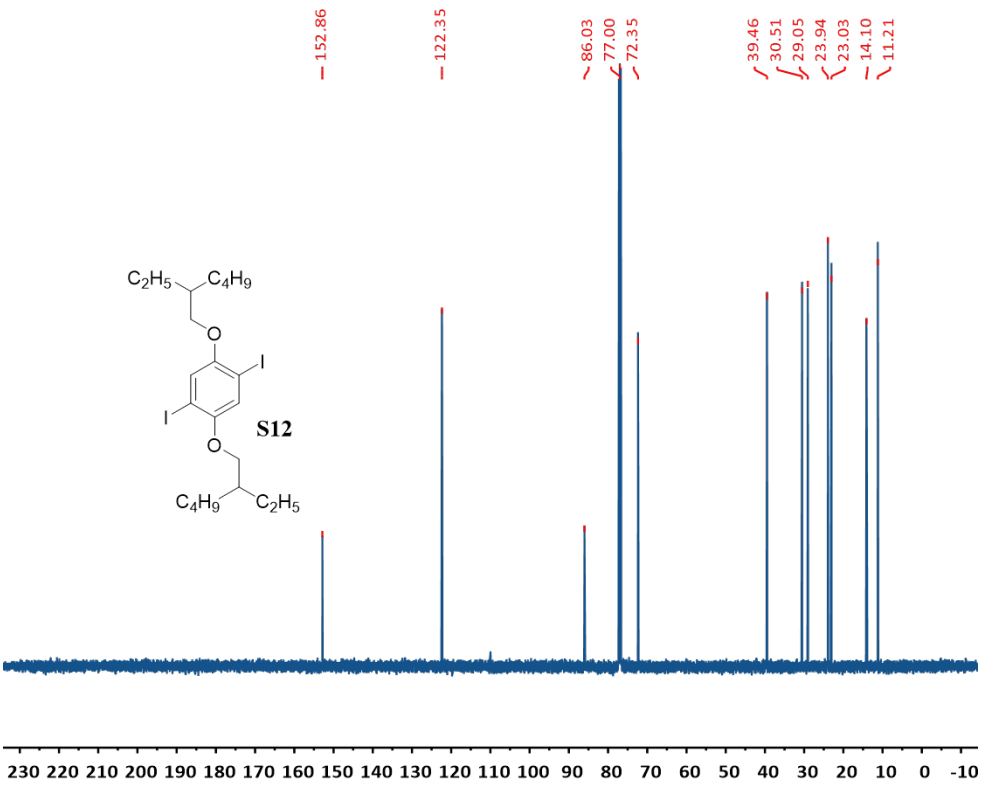
^{13}C NMR of S10 in $CDCl_3$ at 25 °C.



^{1}H NMR of S11 in $CDCl_3$ at 25 °C.

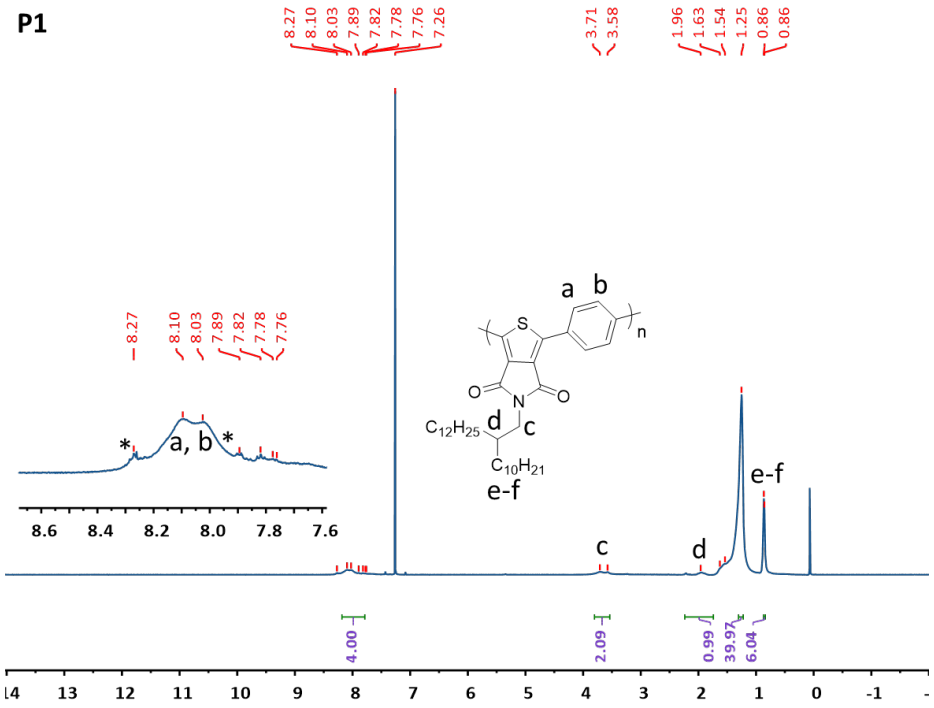


^{1}H NMR of S12 in $CDCl_3$ at 25 °C.

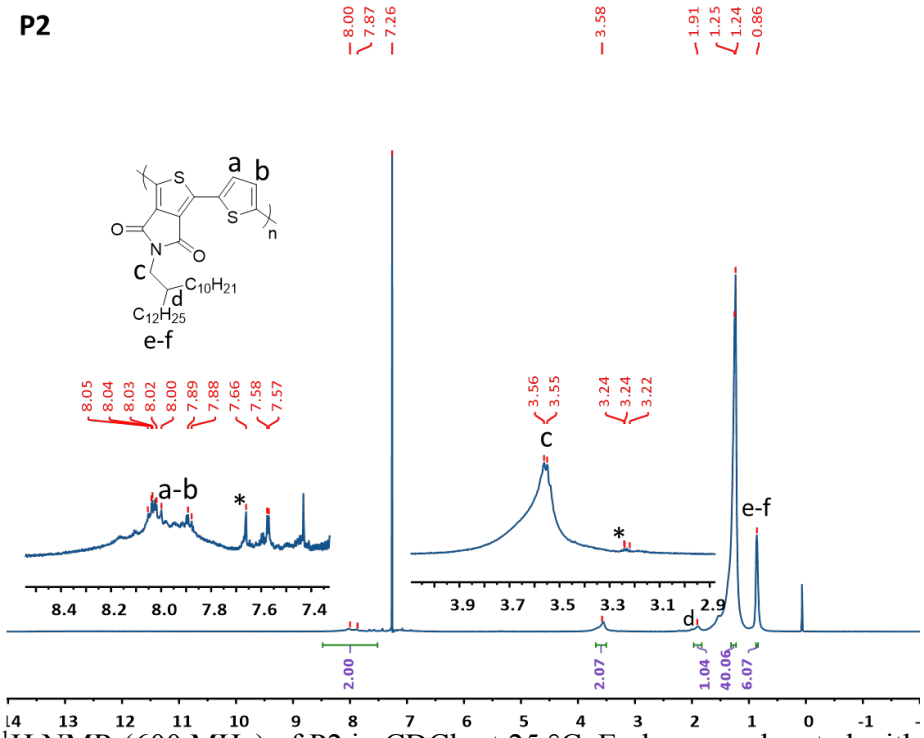


^{13}C NMR of S12 in $CDCl_3$ at 25 °C.

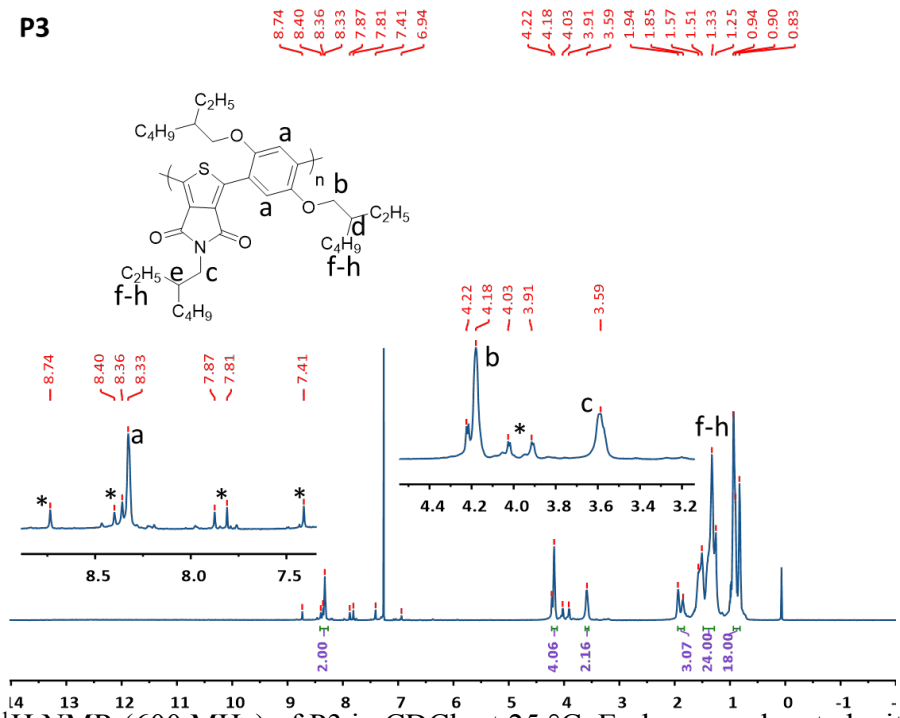
5. Polymer NMR



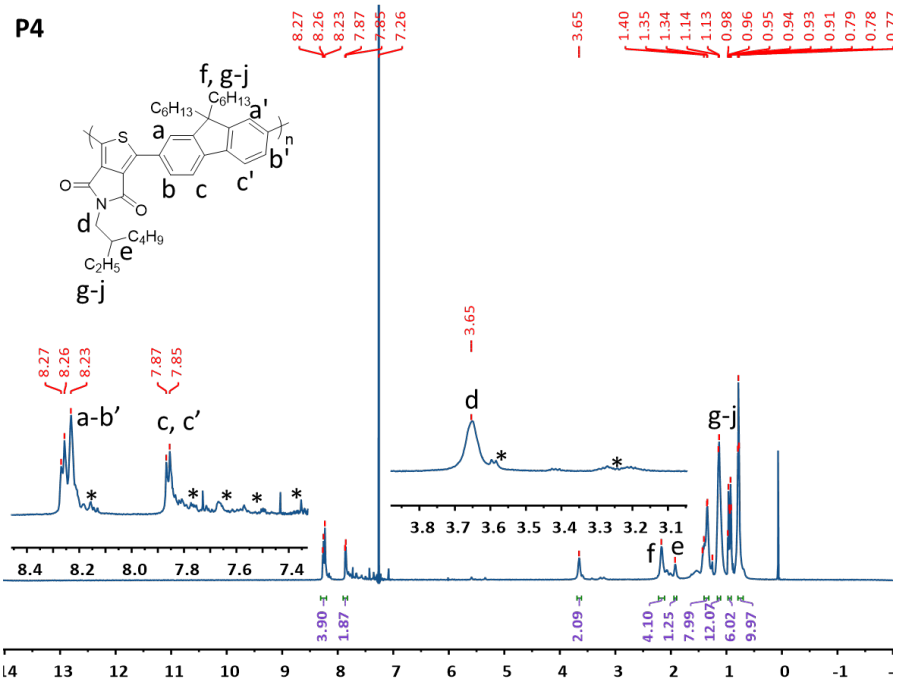
^{1}H NMR (600 MHz) of P1 in $CDCl_3$ at 25 °C. End groups denoted with *. Entry 8 of Table 1.



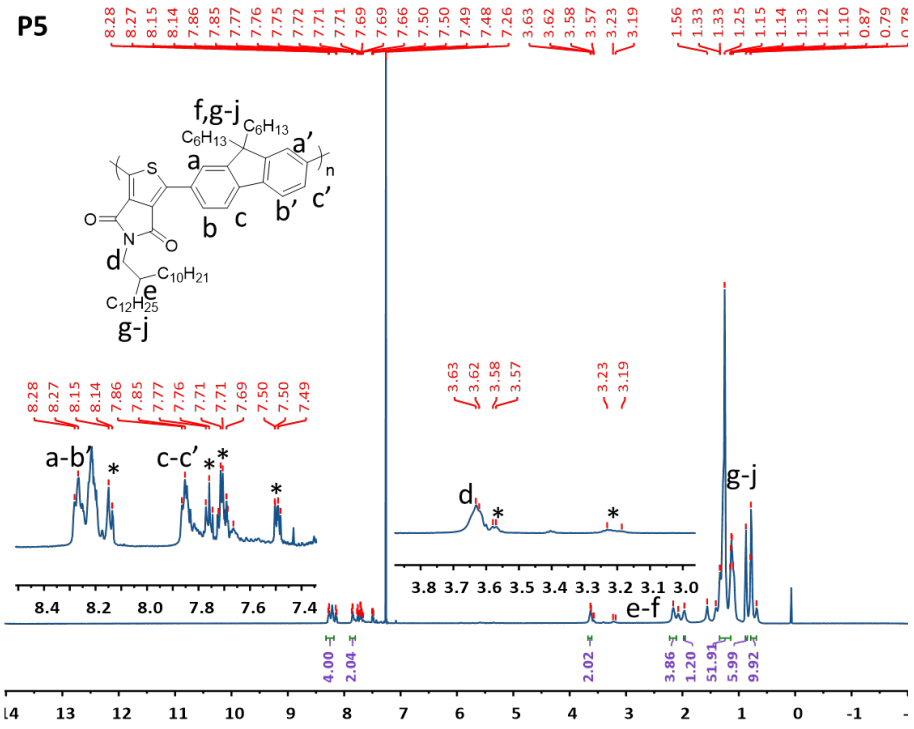
^{1}H NMR (600 MHz) of P2 in $CDCl_3$ at 25 °C. End groups denoted with *. Sample was 2.38 kDa synthesized using DMF since higher M_n samples were only soluble in hot $CHCl_3$ and DCB.



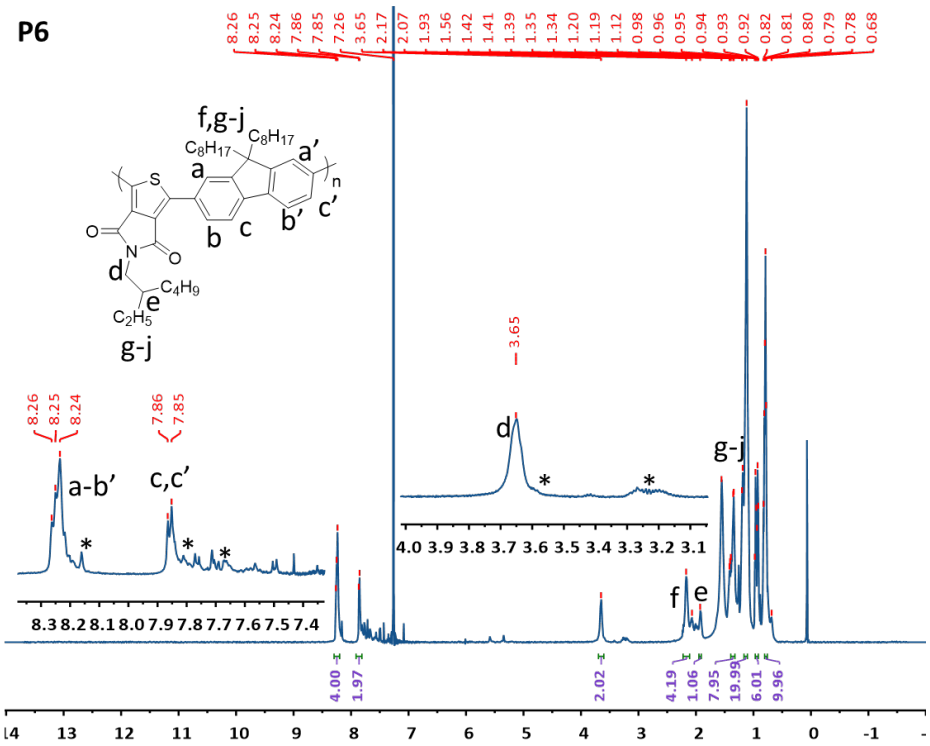
^{1}H NMR (600 MHz) of P3 in $CDCl_3$ at 25 °C. End groups denoted with *. Entry P3 of Table 2.



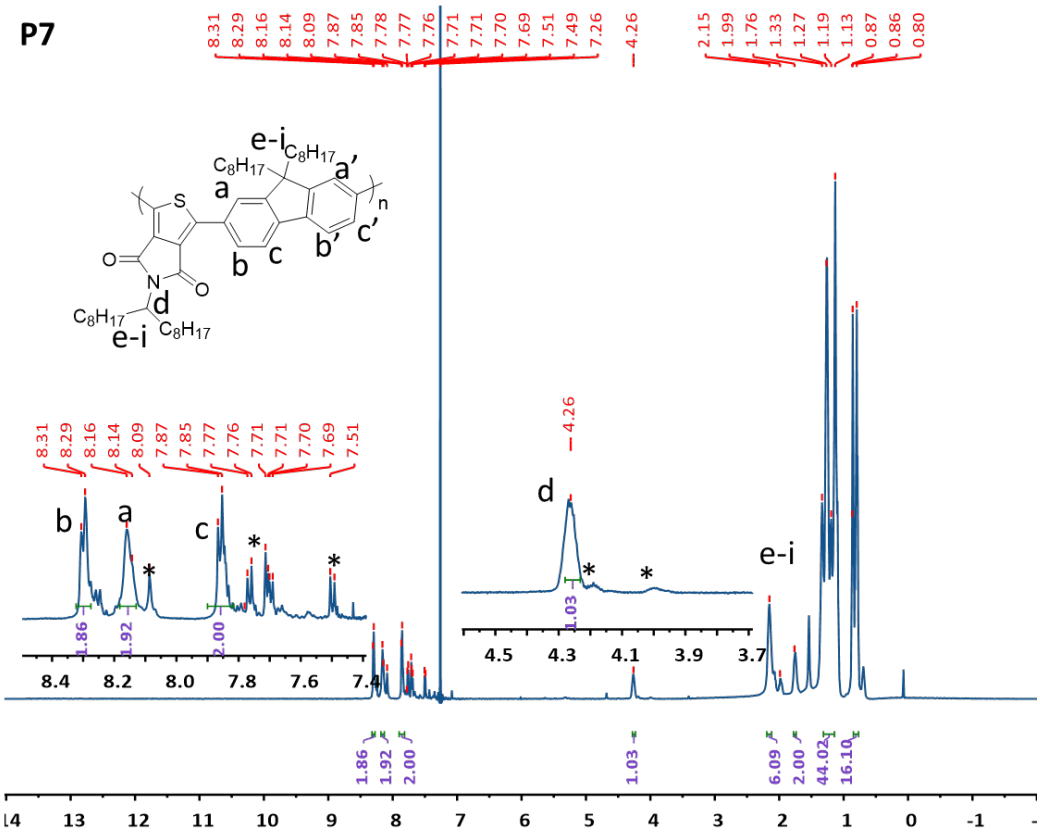
^{1}H NMR (600 MHz) of P4 in $CDCl_3$ at 25 °C. End groups denoted with *. Entry P4 of Table 2.



^{1}H NMR (600 MHz) of P5 in $CDCl_3$ at 25 °C. End groups denoted with *. Entry P5a of Table 2.



^{1}H NMR (600 MHz) of P6 in $CDCl_3$ at 25 °C. End groups denoted with *. Entry P6a of Table 2.



^{1}H NMR (600 MHz) of P7 in $CDCl_3$ at 25 °C. End groups denoted with *. Entry P7 of Table 2.

6. Figure S1: Proposed Catalytic Cycles for Cu-DArP

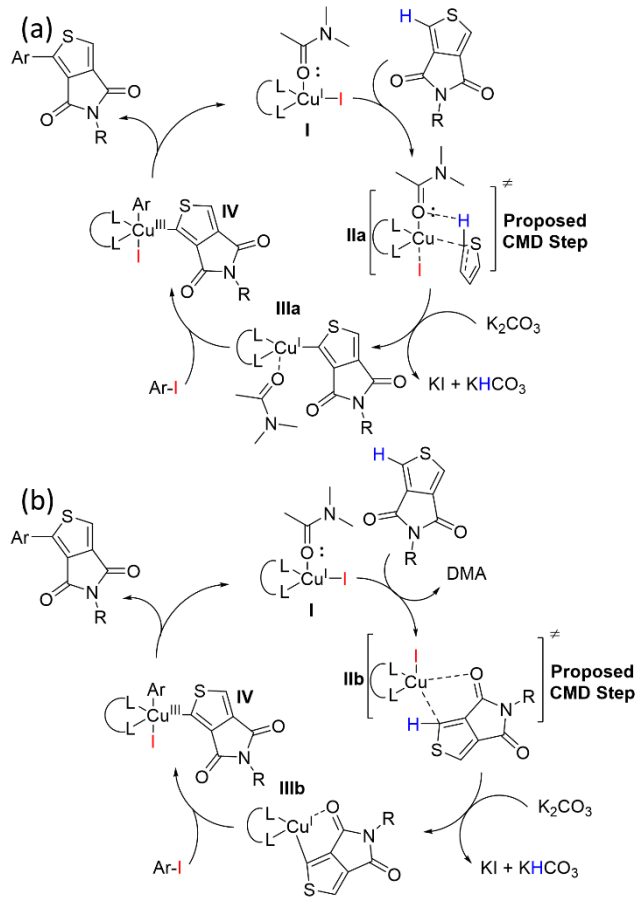


Figure S1. Proposed catalytic cycles (a) and (b) for the Cu-catalyzed DArP where the bidentate ligand is phenanthroline. TPD is simplified as a thiophene (IIa) for clarity.

Based on the results from the optimization of polymerization conditions for P1 and the polymerization outcomes for the polymers listed in Table 2, some insight regarding potential mechanisms can be gained. The proposed mechanisms, shown in Figure S1a and S1b, are based on the experimental findings reported here and previous work regarding Cu-catalyzed arylations.[15–19] However, continuing work to support either pathway is still ongoing. Specifically, it was found that solvent, base, and monomer sterics were critical factors for the polymerization. The effect of solvent and base may be due to their participation in a concerted-metallation-deprotonation (CMD) step (II), shown in Figure S1a, and where the solvent potentially participates

as a stabilizing ligand throughout the catalytic cycle (I and IIIa). The transition state for the CMD step and the oxidative addition step to form IV would require displacement of the amide solvent, and this could largely be inhibited through steric interactions from coordinating or approaching monomers due to the alkyl substituents. Conversely, it is possible the carbonyl of the TPD functions as a directing-group affording IIb and IIIb (Figure S1b). In regards to both of the proposed catalytic cycles, it is plausible that an equilibrium exists between the species IIIa and IIIb before the formation of IV.

8. References

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