

Supporting Information

Tin-free synthesis of a ternary random copolymer for BHJ solar cells: Direct (Hetero)Arylation
versus Stille polymerization

G. Marzano,^a D. Kotowski,^b F. Babudri,^a R. Musio,^a A. Pellegrino,^c S. Luzzati,^b R. Po,^c

G.M. Farinola^{*a}

^a Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, Via Orabona 4, 70125, Italy

Fax: +39 0805442064

E-mail: gianluca maria.farinola@uniba.it

^b Consiglio Nazionale delle Ricerche, CNR, Istituto per lo Studio delle Macromolecole, ISMAC,
Milan, Italy

^c Centro Ricerche per le Energie Rinnovabili e l'Ambiente – Istituto Eni Donegani, Eni SpA, Via
Fauser 4, 28100 Novara, Italy

INDEX

- 1. Synthetic complexity (SC) table of the copolymer P**
- 2. Spectroscopic and optical characterization of oligomers and polymers**
- 3. Device characterization**

1. Synthetic complexity (SC) table of the copolymer P

Table S1. Number of synthetic steps (NSS), reciprocal yield (RY), number of operation units for the isolation/purification (NUO), number of column chromatographies for the isolation/purification (NCC) and number of hazardous chemicals (NHC) for polymers *via* Stille (P_{STILLE}) and Direct (Hetero)Arylation (P_{DA}) Polymerization. Synthetic complexity (SC) is calculated according to the method reported in ref. 2

	Compound	NSS	RY	NUO	NCC	NHC	SC
Monomers	4	4	3.03	8	1	7	-
	7	5	3.70	11	1	15	-
	5	1	1.05	2	0	4	-
	6	3	2.17	9	2	10	-
Polymers	P_{STILLE}	10	6.92	22	3	29	45.3
	P_{DA}	9	6.25	19	3	21	40.1

2. Spectroscopic and optical characterization of oligomers and polymers

^1H NMR (CDCl_3 , 500 MHz)

F2

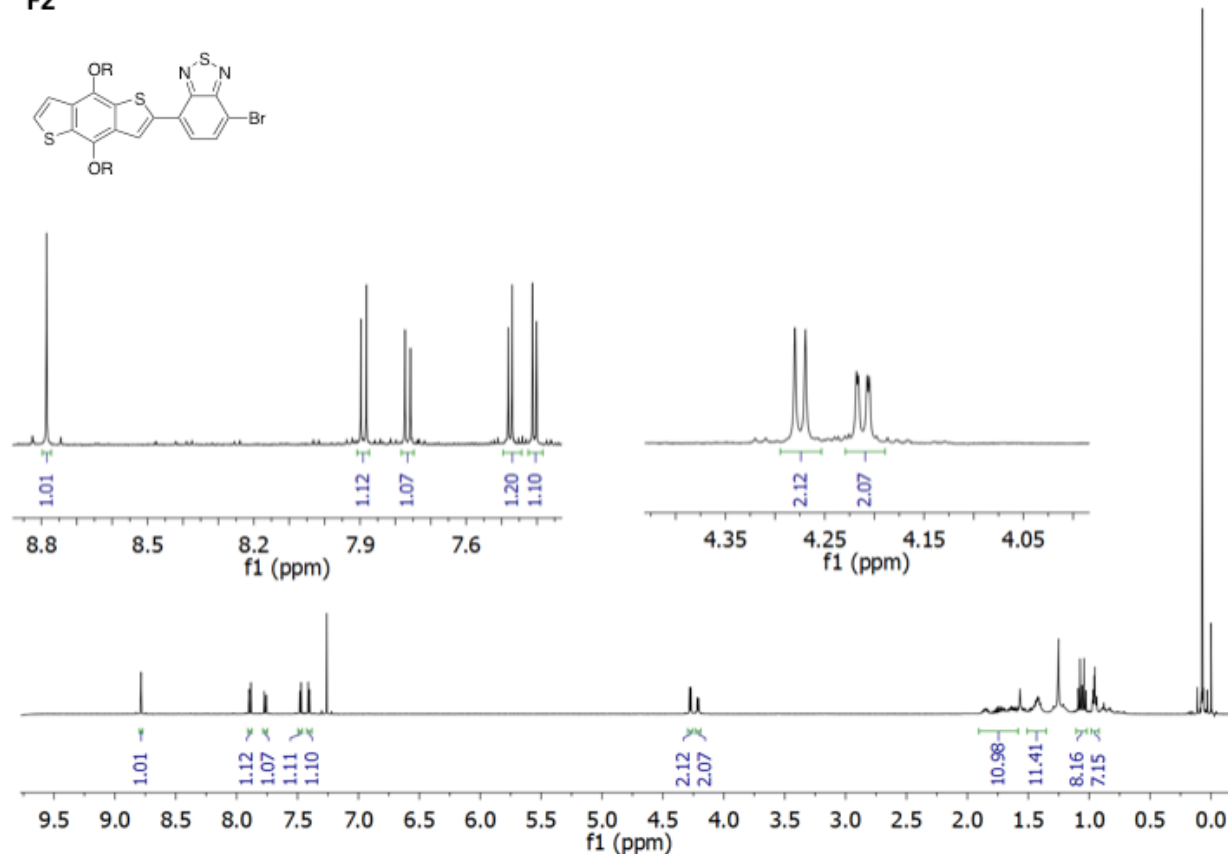


Figure S1. ^1H NMR spectrum of 4-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)-7-bromobenzo[c][1,2,5]thiadiazole (**F2**)

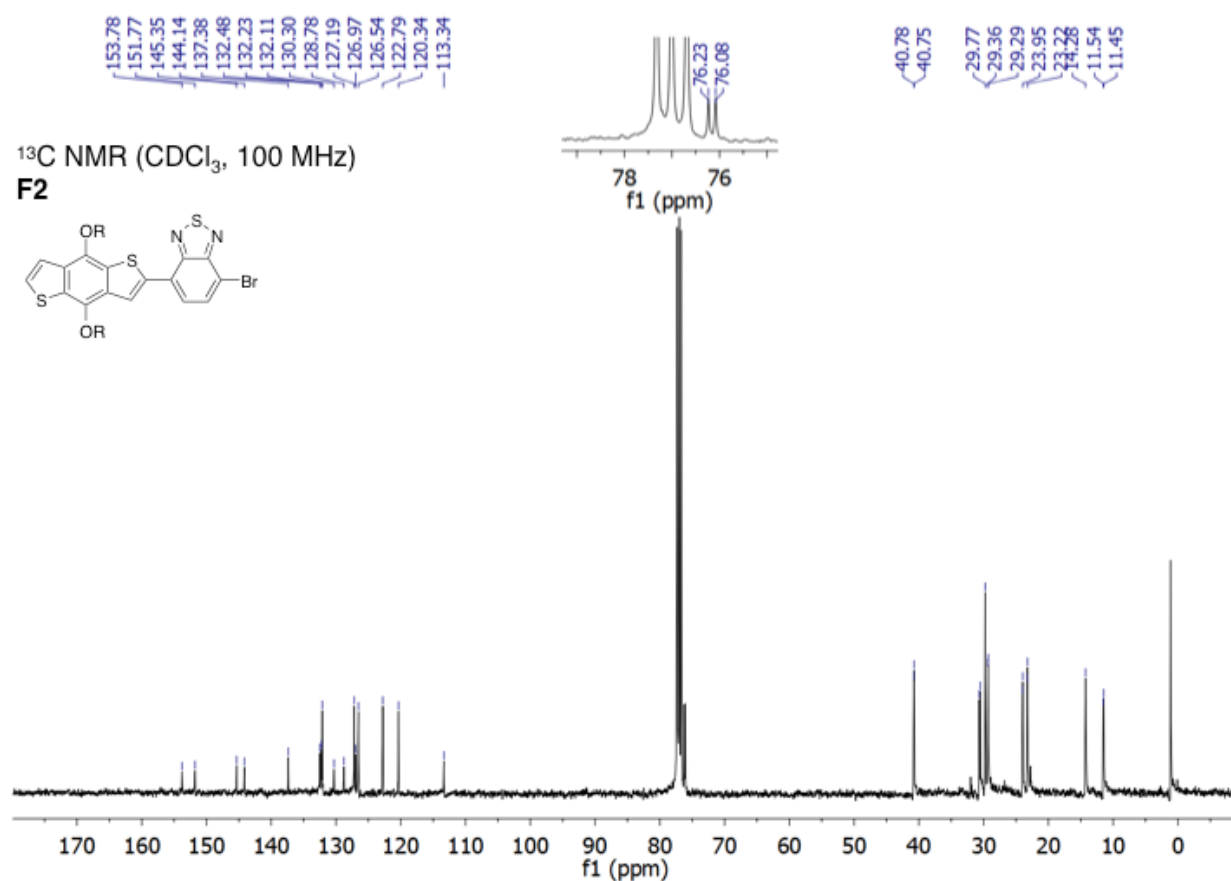


Figure S2. ¹³C NMR spectrum of 4-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)-7-bromobenzo[c][1,2,5]thiadiazole (**F2**)

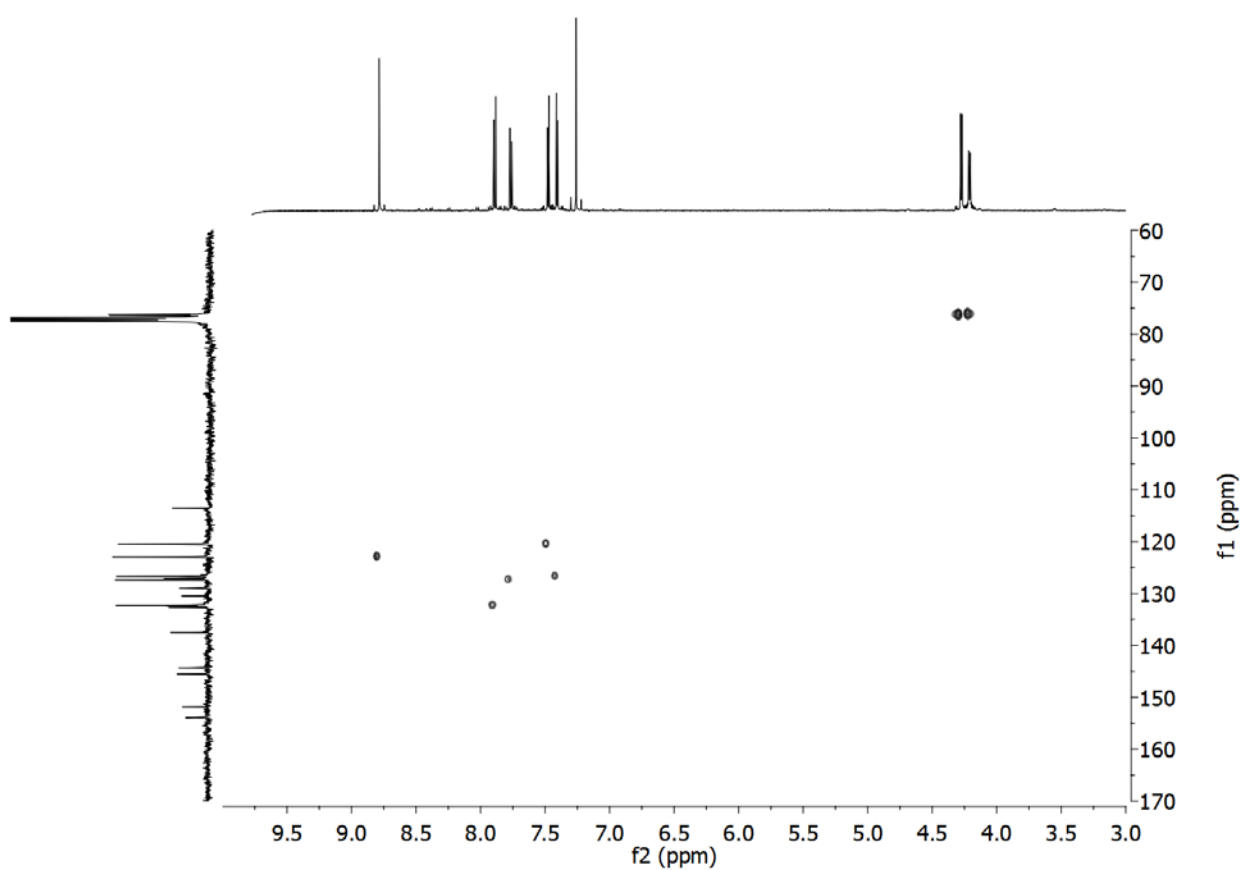


Figure S3. ^1H - ^{13}C HSQC spectrum of 4-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)-7-bromobenzo[c][1,2,5]thiadiazole (**F2**) in the region 60-170 ppm (f1) and 3.0-10.0 ppm (f2)

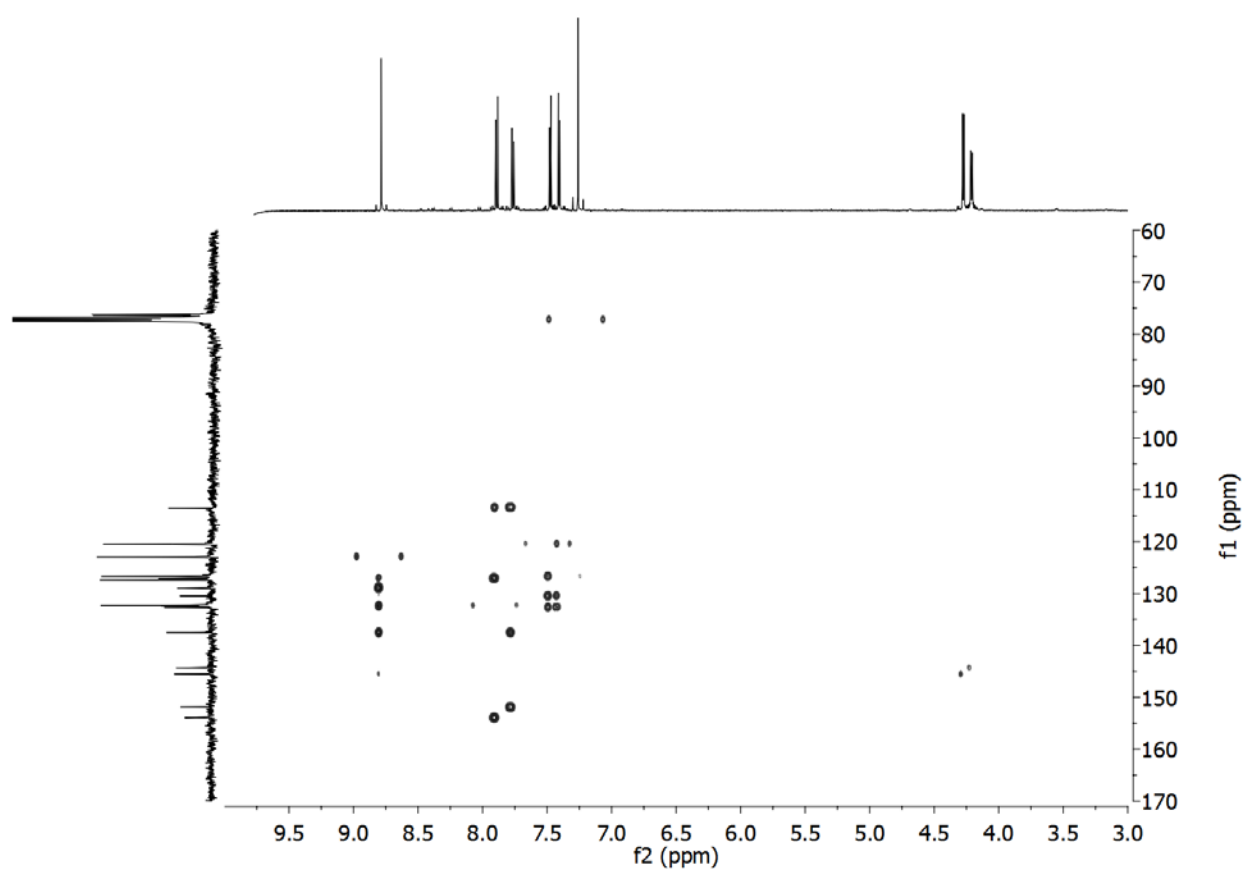


Figure S4. ^1H - ^{13}C HMBC spectrum of 4-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)-7-bromobenzo[c][1,2,5]thiadiazole (**F2**) in the region 60-170 ppm (f1) and 3.0-10.0 ppm (f2)

^1H NMR (CDCl_3 , 500 MHz)

F3

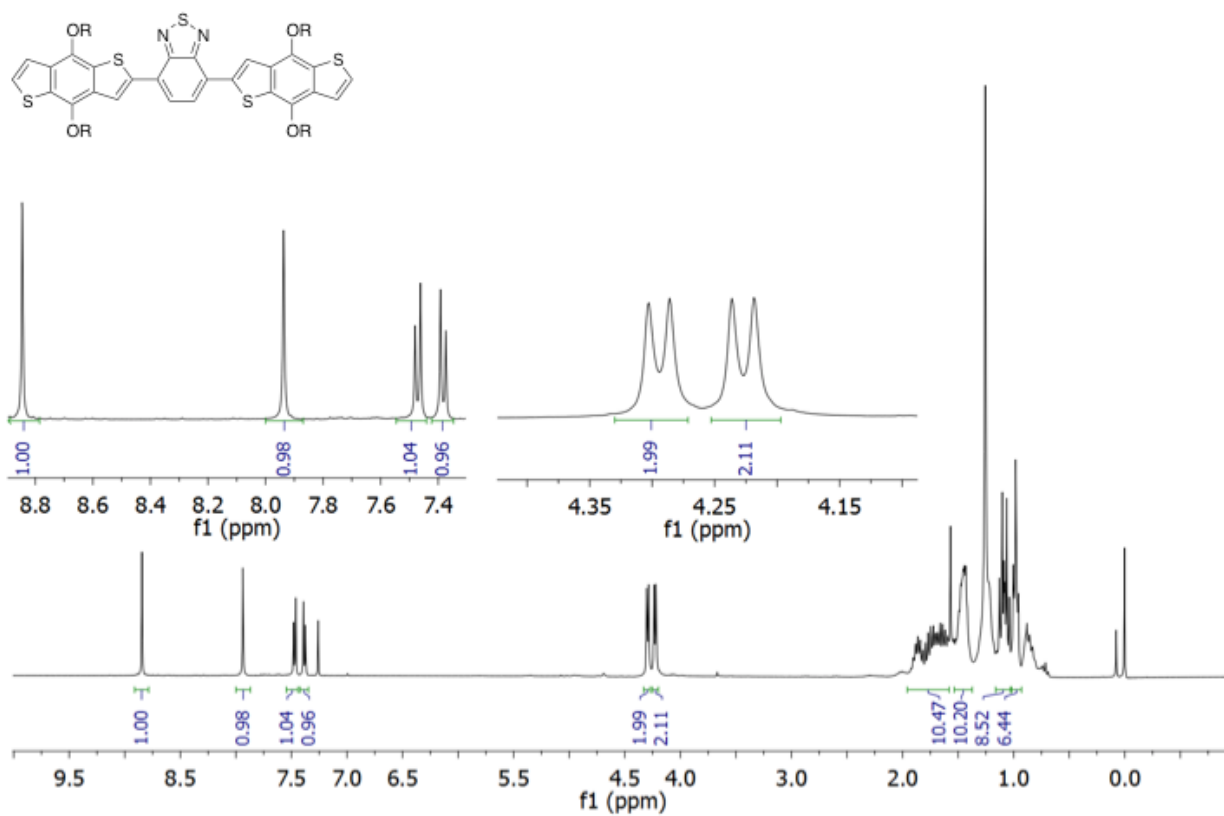


Figure S5. ^1H NMR spectrum of 4,7-bis(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**F3**)

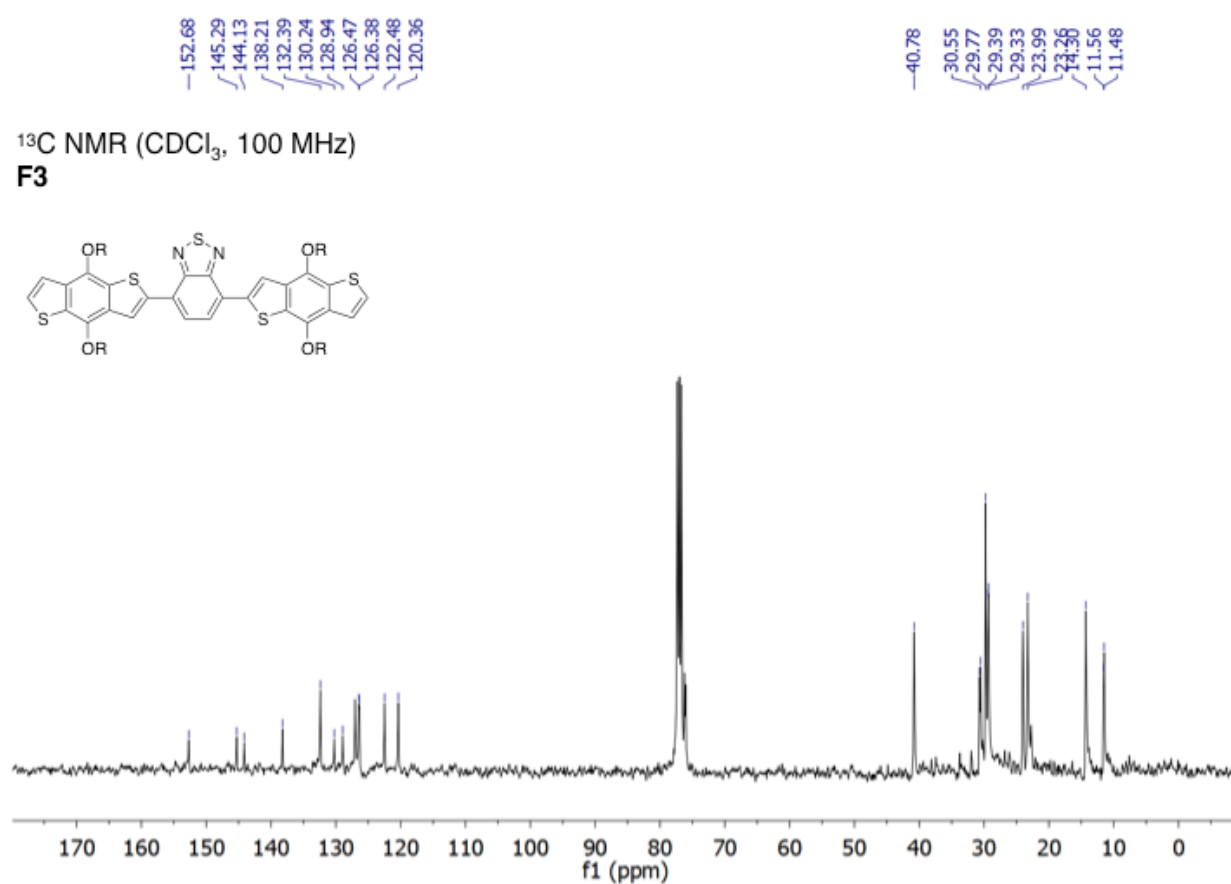


Figure S6. ¹³C NMR spectrum of 4,7-bis(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**F3**)

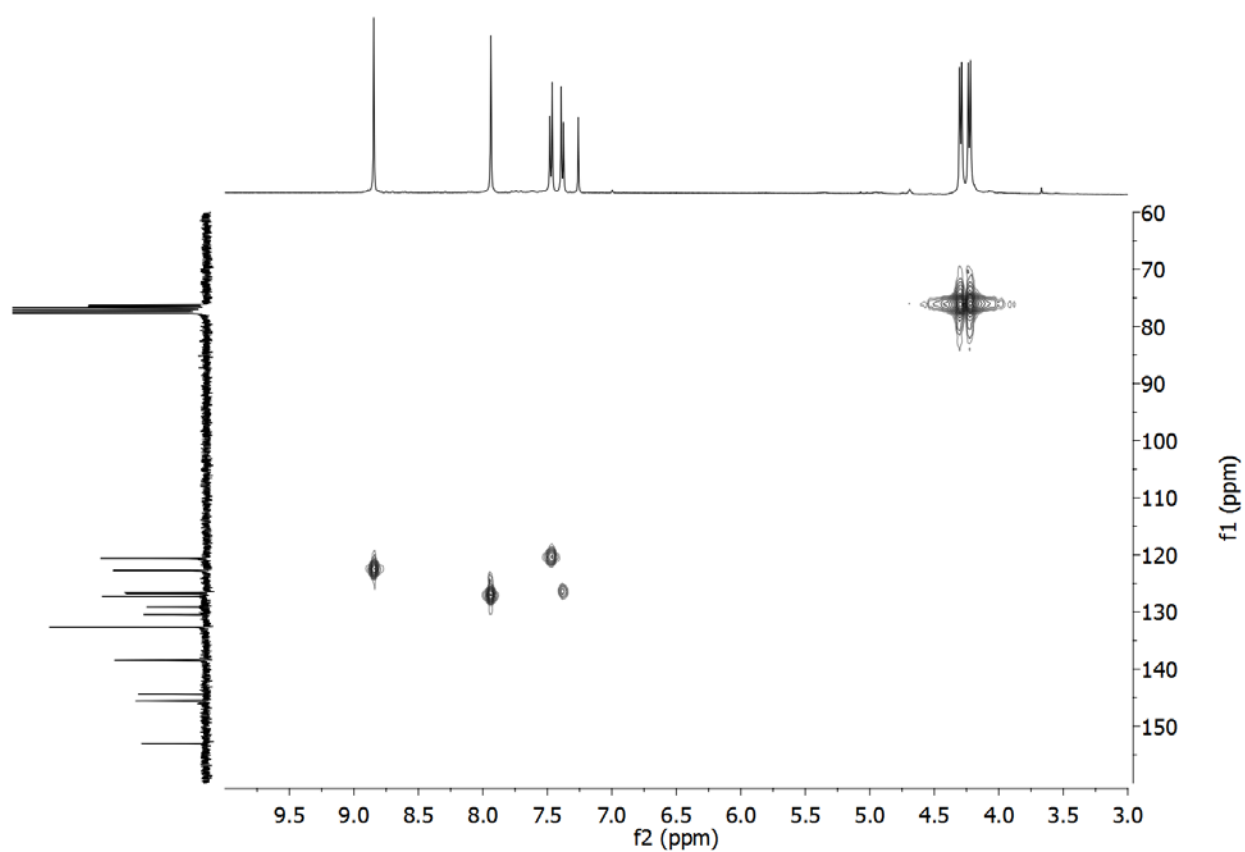


Figure S7. ^1H - ^{13}C HSQC spectrum of 4,7-bis(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**F3**) in the region 60-170 ppm (f1) and 3.0-10.0 ppm (f2)

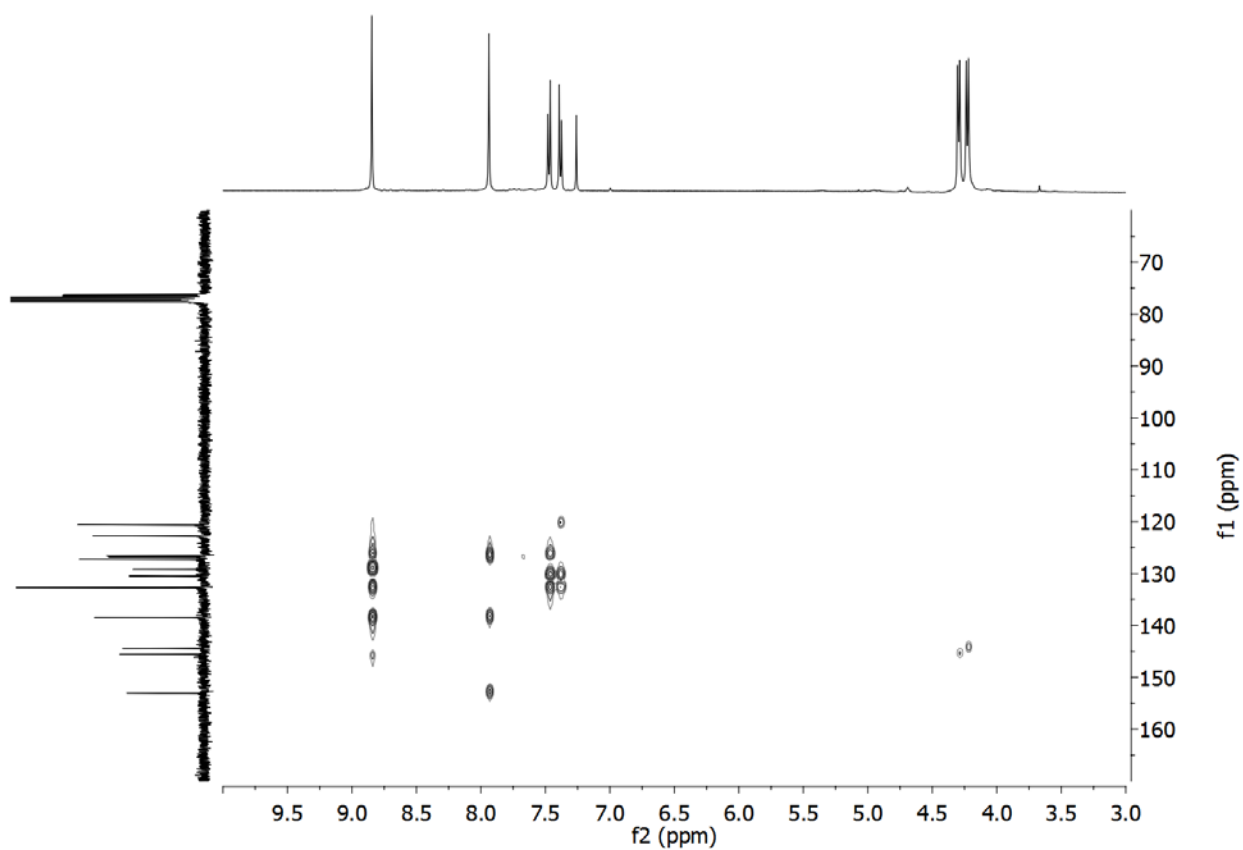


Figure S8. ^1H - ^{13}C HMBC spectrum of 4,7-bis(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**F3**) in the region 60-170 ppm (f_1) and 3.0-10.0 ppm (f_2)

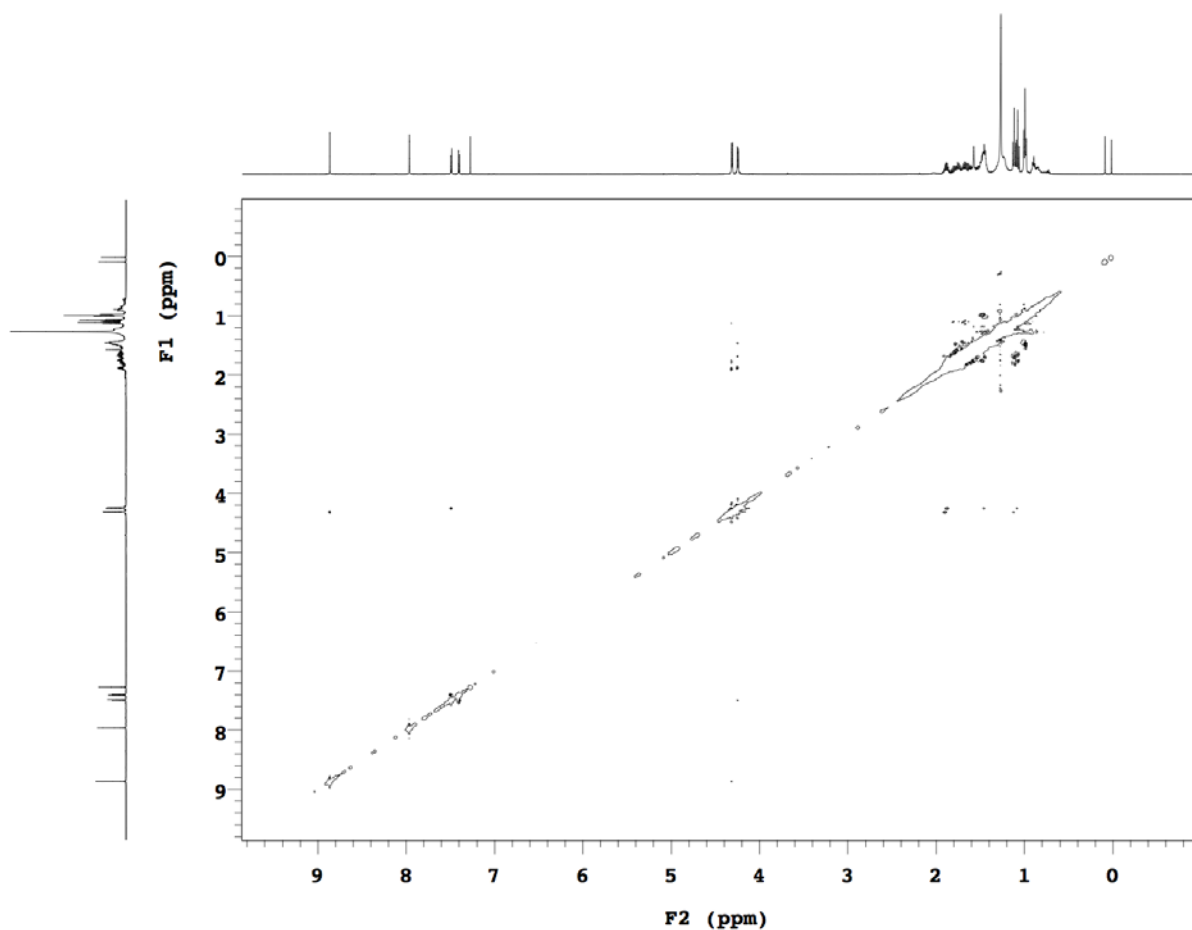


Figure S9. ^1H - ^1H NOESY spectrum of 4,7-bis(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**F3**)

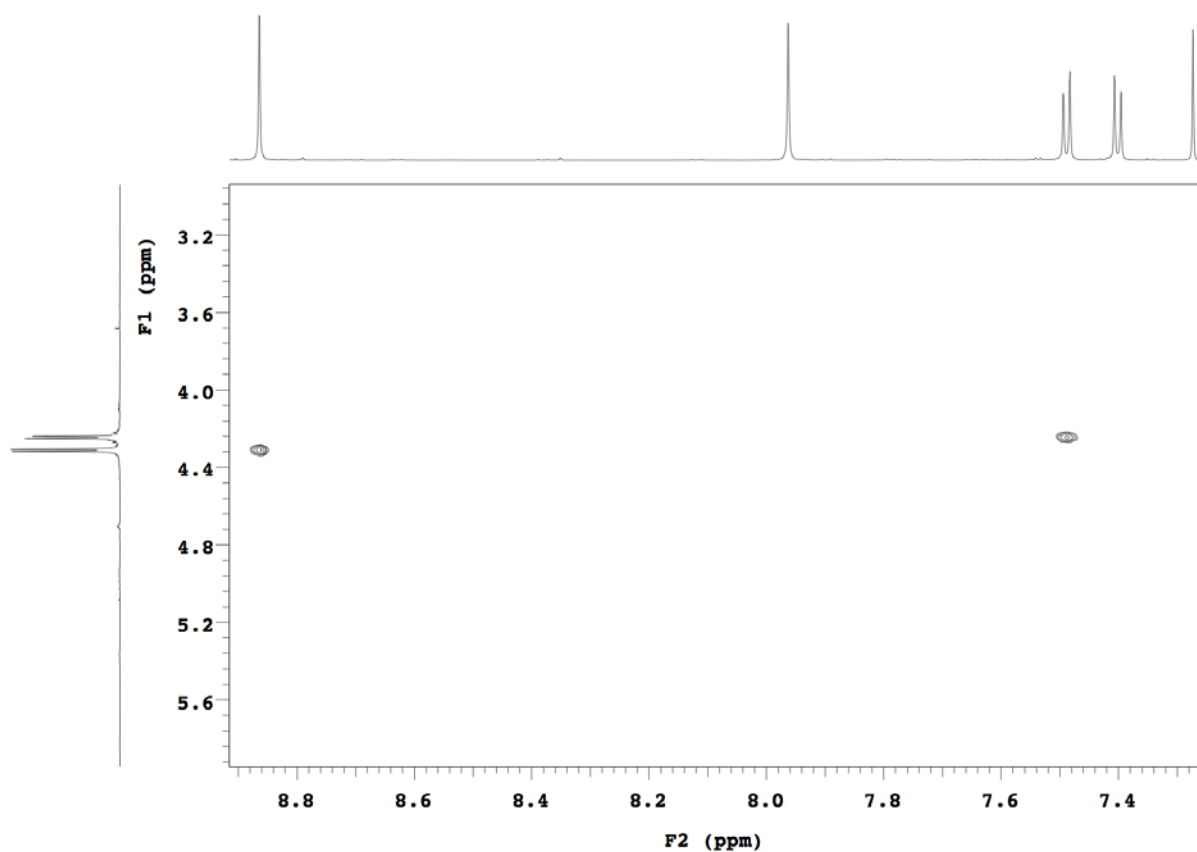


Figure S9a. Expansion of 2D NOESY spectrum of F3 showing the cross region of OCH₂/thienyl protons of the benzodithiophene moiety.

^1H NMR (CDCl_3 , 500 MHz)

F4

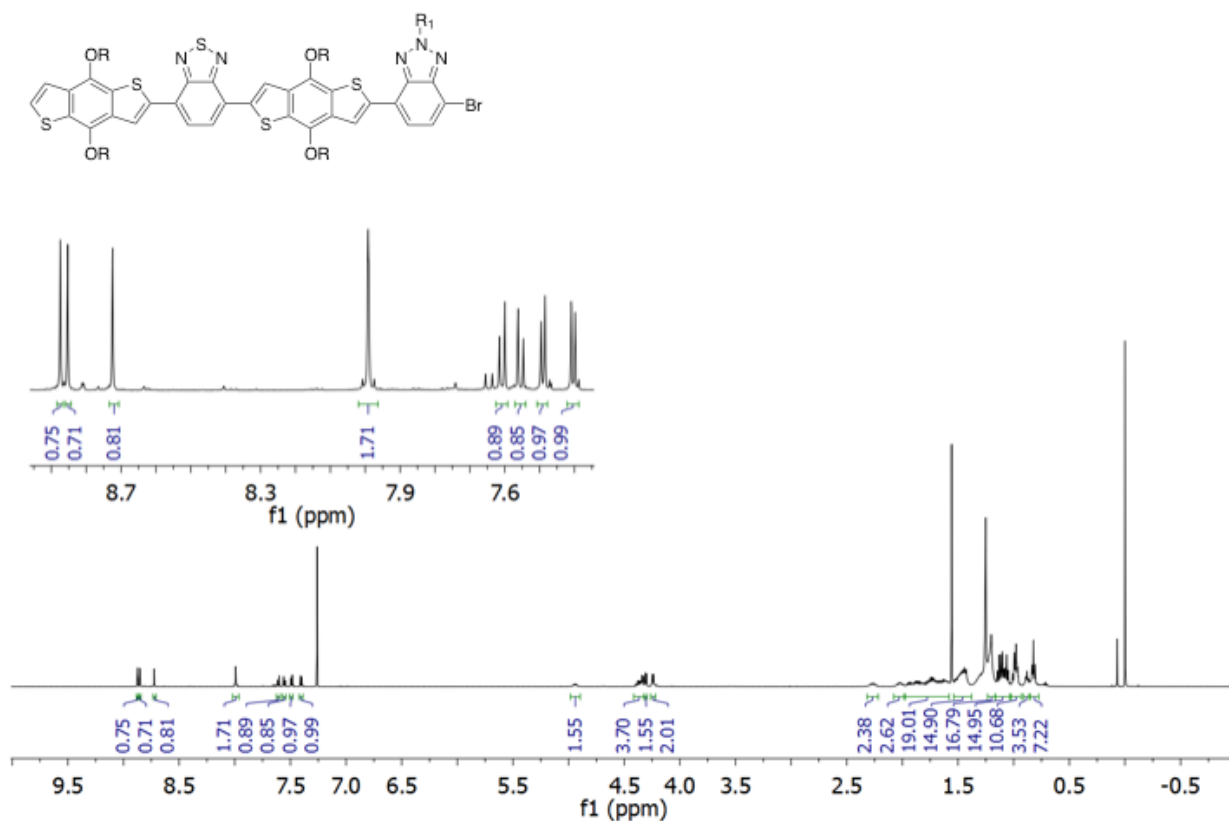


Figure S10. ^1H NMR spectrum of 4-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)-7-(6-(7-bromo-2-(heptadecan-9-yl)-2*H*-benzo[*d*][1,2,3]triazol-4-yl)-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**F4**)

¹³C NMR (CDCl₃, 100 MHz)

F4

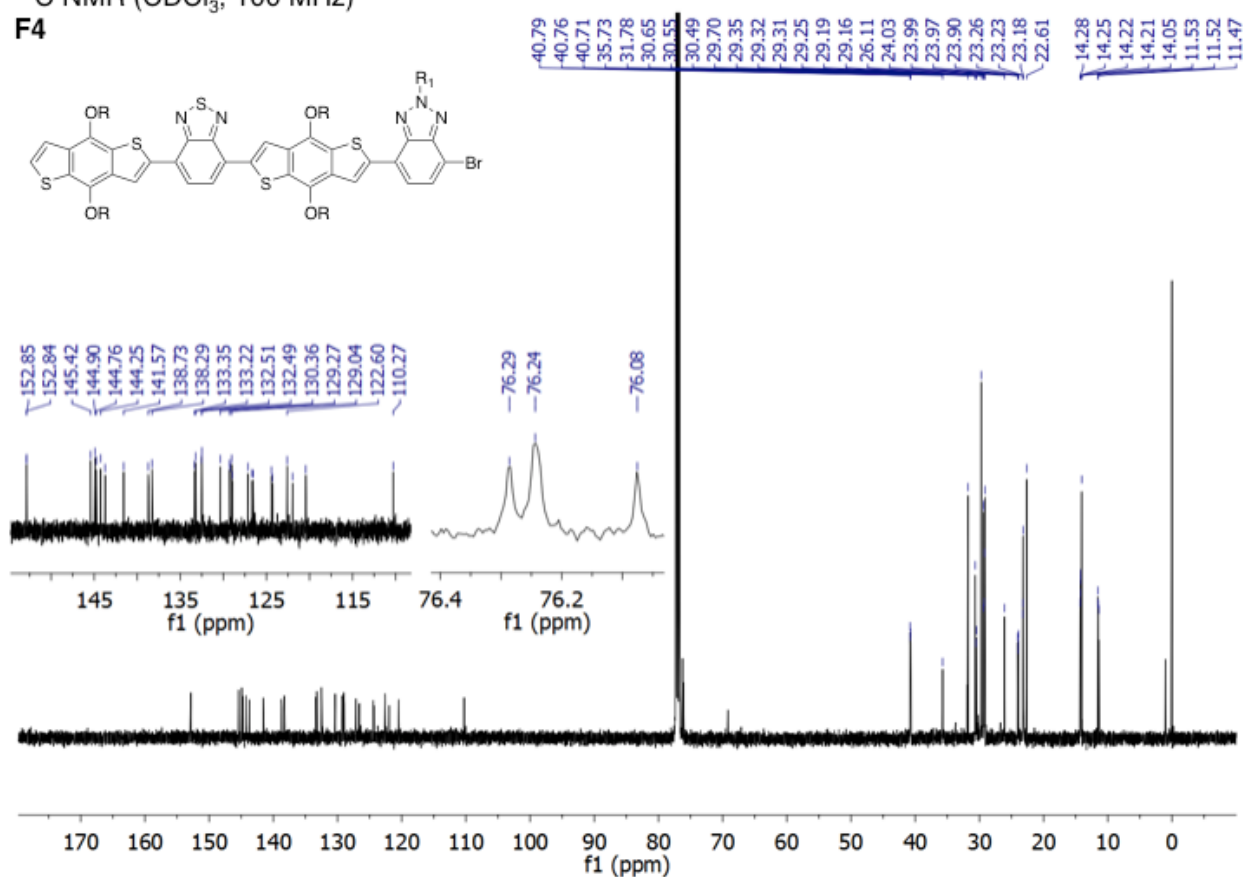


Figure S11. ¹³C NMR spectrum of 4-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)-7-(6-(7-bromo-2-(heptadecan-9-yl)-2*H*-benzo[*d*][1,2,3]triazol-4-yl)-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**F4**)

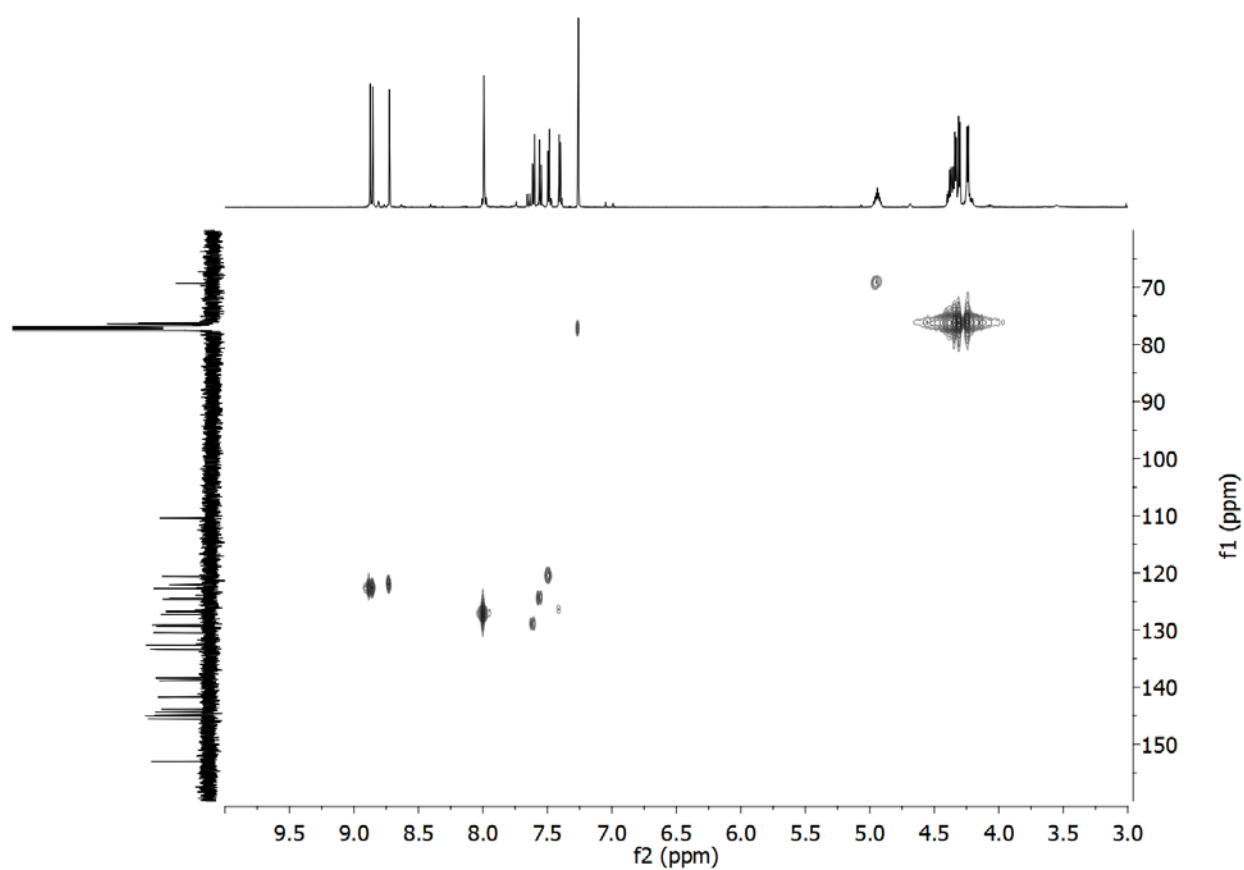


Figure S12. ^1H - ^{13}C HSQC spectrum of 4-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)-7-(6-(7-bromo-2-(heptadecan-9-yl)-2*H*-benzo[*d*][1,2,3]triazol-4-yl)-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**F4**) in the region 60-170 ppm (f1) and 3.0-10.0 ppm (f2)

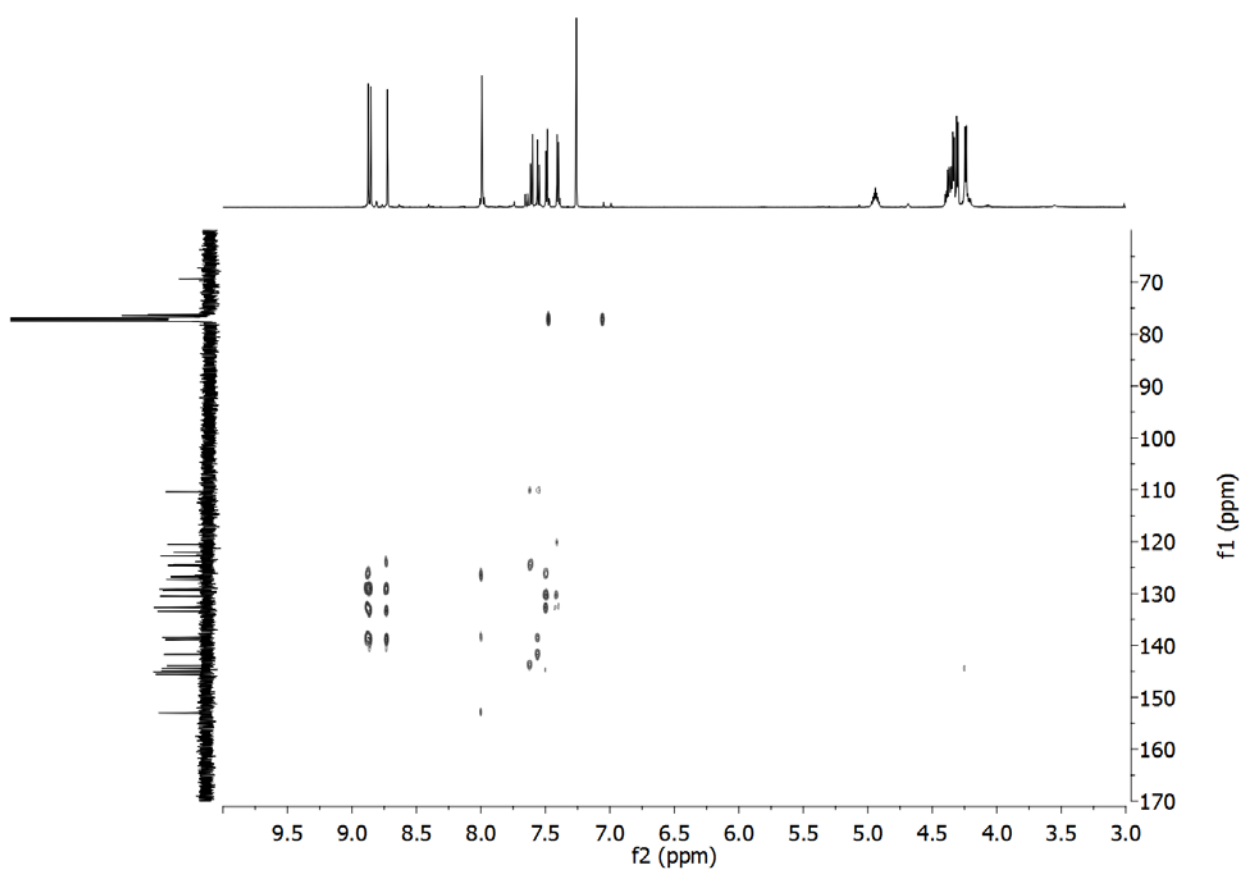


Figure S13. ^1H - ^{13}C HMBC spectrum of 4-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)-7-(6-(7-bromo-2-(heptadecan-9-yl)-2*H*-benzo[*d*][1,2,3]triazol-4-yl)-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**F4**) in the region 60-170 ppm (f1) and 3.0-10.0 ppm (f2)

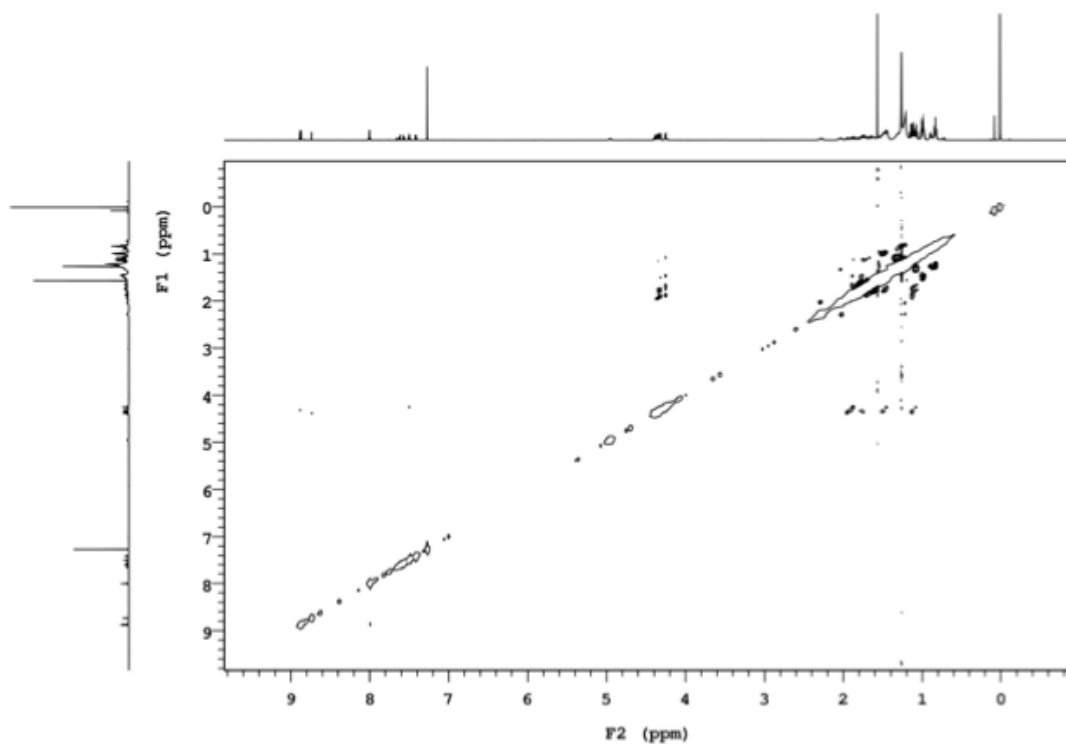


Figure S14. ^1H - ^1H NOESY spectrum of 4,7-bis(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**F4**)

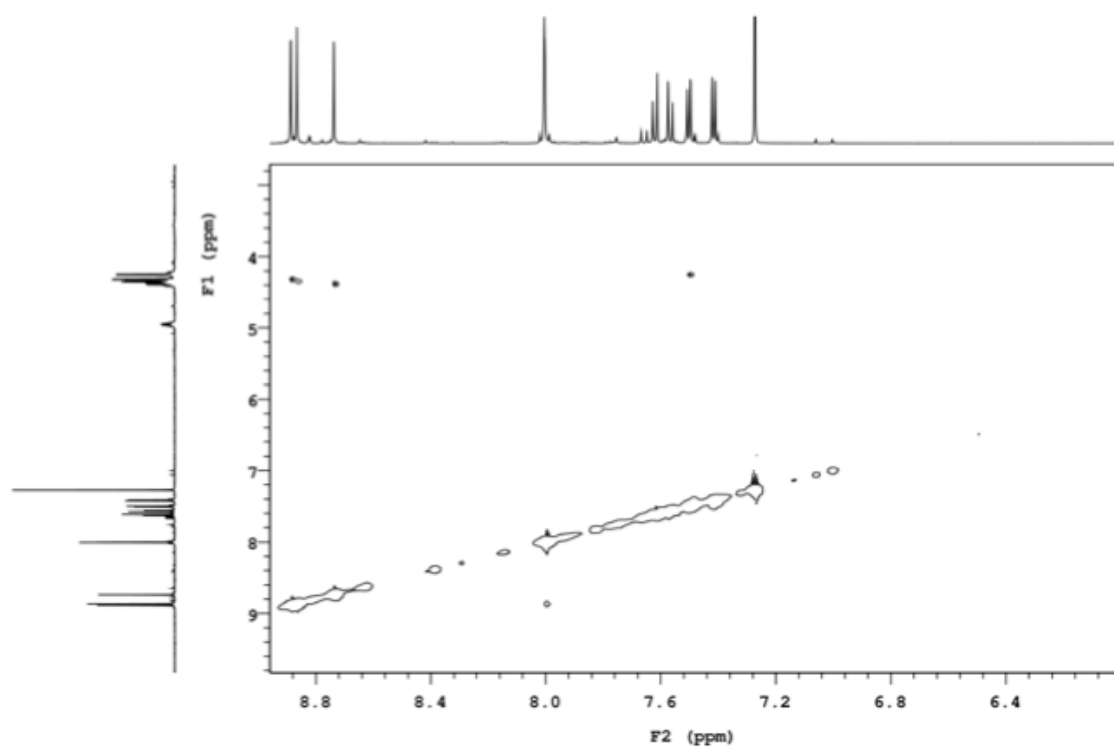


Figure S14a. Expansion of 2D NOESY spectrum of F4 showing the cross region of OCH₂/thienyl protons of the benzodithiophene moiety.

¹H NMR (CDCl₃, 500 MHz)

F5

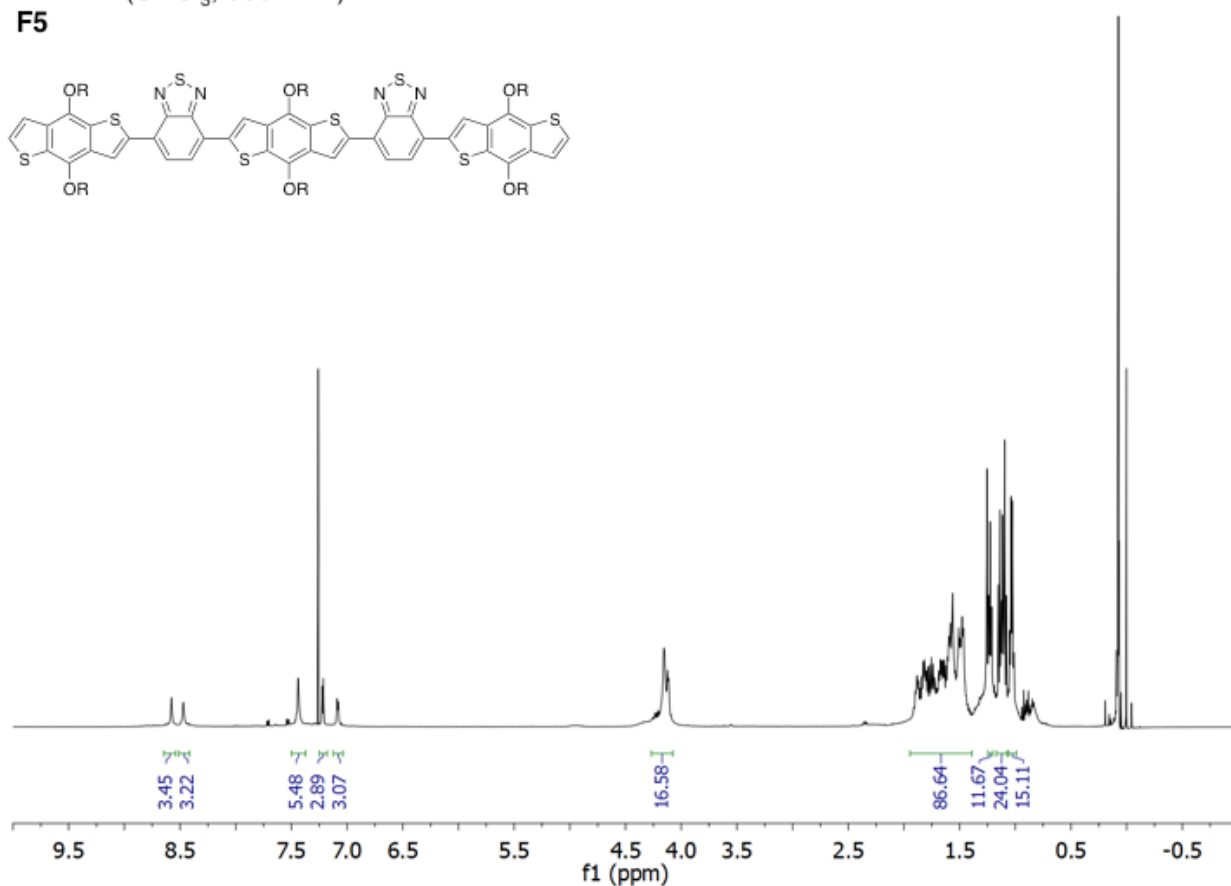


Figure S15. ¹H NMR spectrum of 7,7'-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(4-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole) (**F5**)

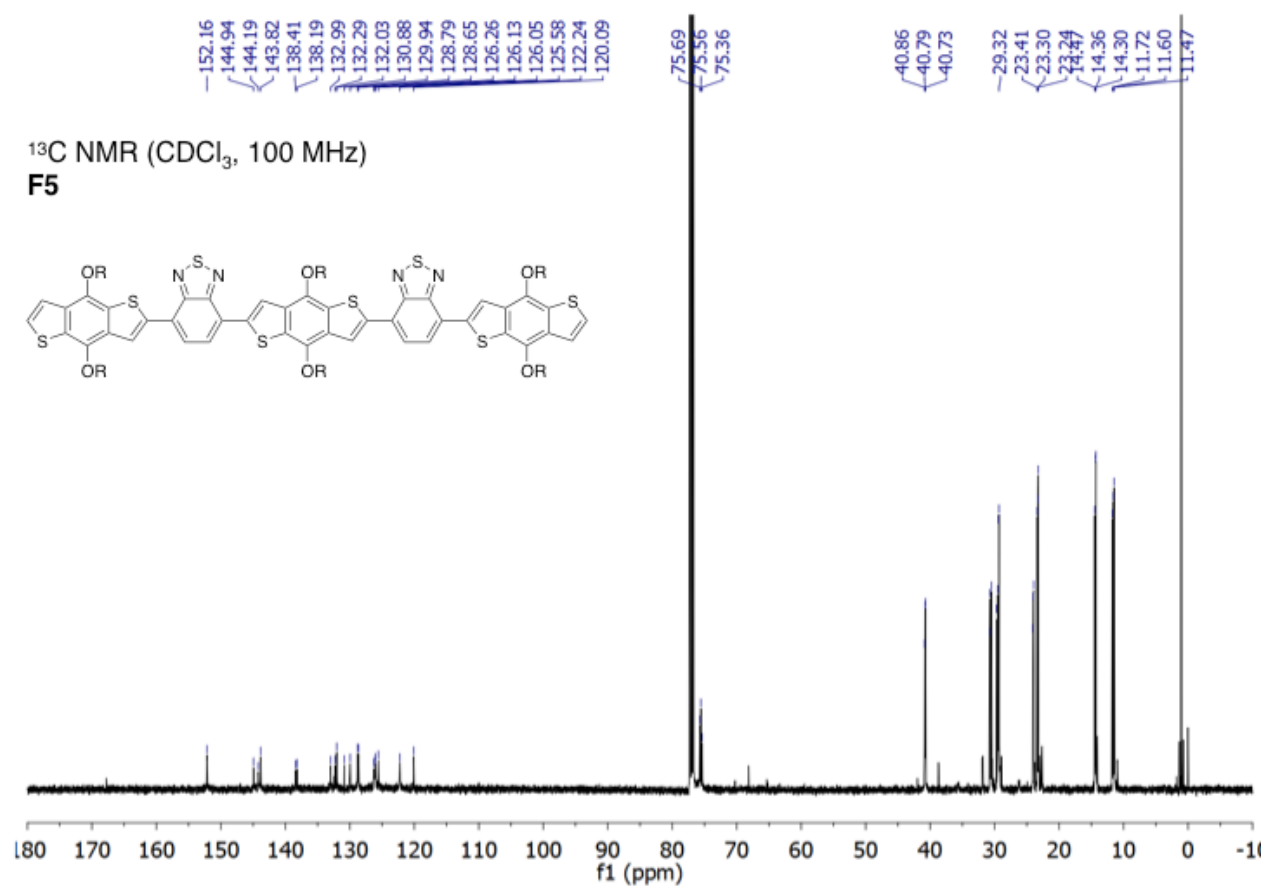


Figure S16. ¹³C NMR spectrum of 7,7'-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(4-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole) (**F5**)

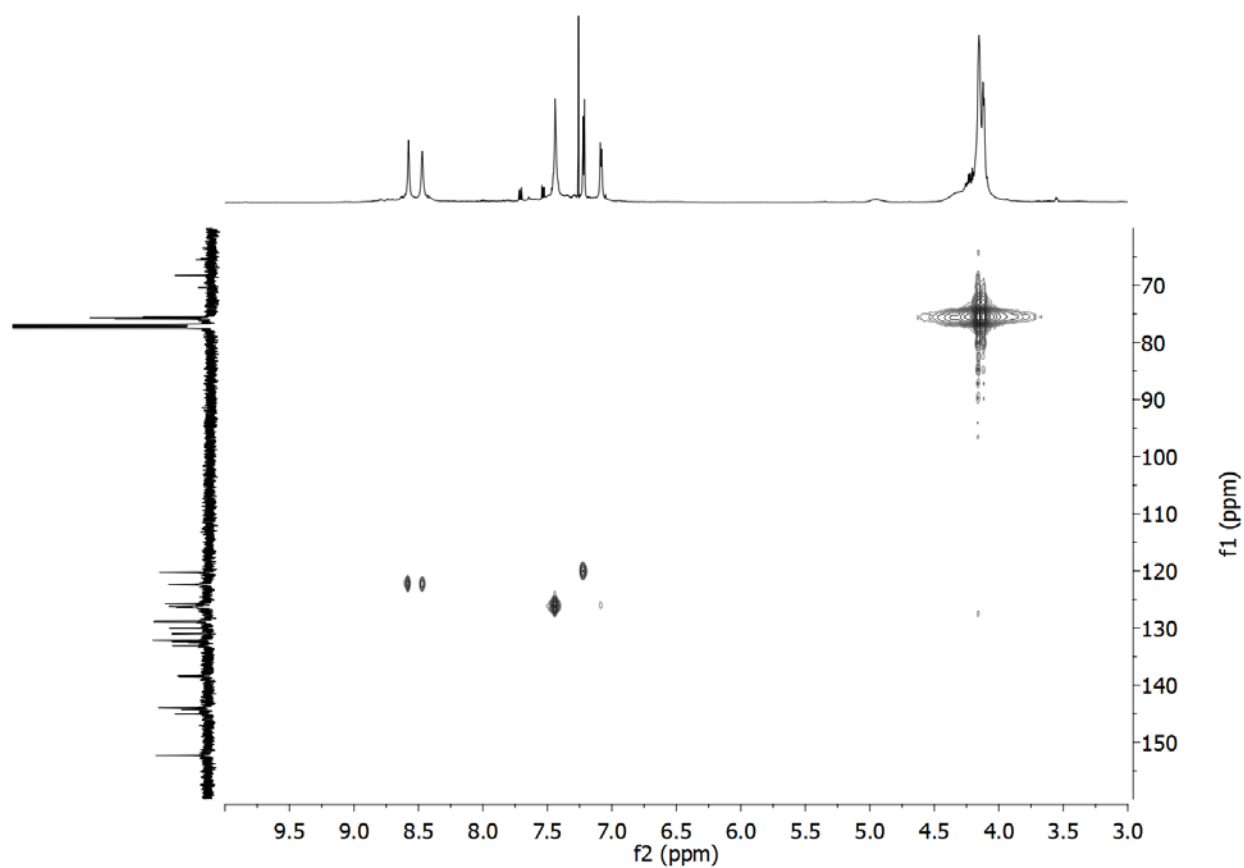


Figure S17. ^1H - ^{13}C HSQC spectrum of 7,7'-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(4-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole) (**F5**) in the region 60-170 ppm (f1) and 3.0-10.0 ppm (f2)

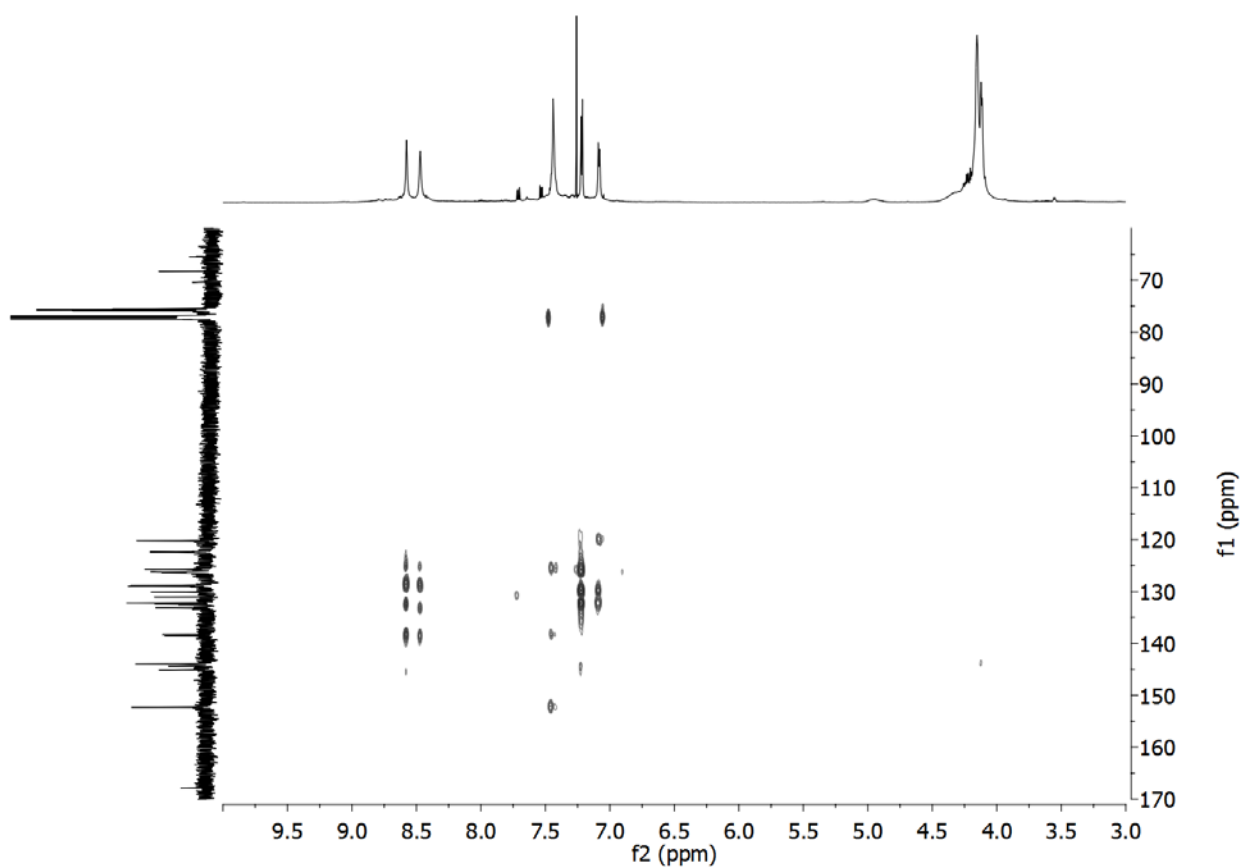


Figure S18. ^1H - ^{13}C HMBC spectrum of 7,7'-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(4-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole) (**F5**) in the region 60-170 ppm (f1) and 3.0-10.0 ppm (f2)

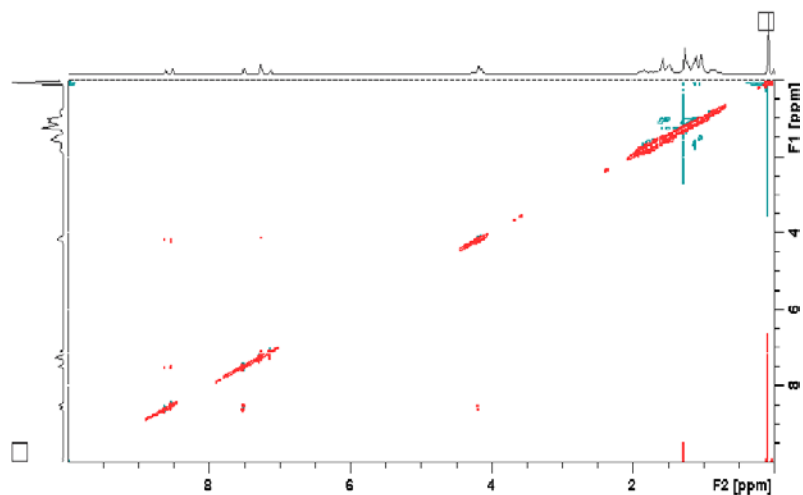


Figure S19. ^1H - ^1H NOESY spectrum of 7,7'-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(4-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole) (**F5**)

^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz)

P_{DA}2

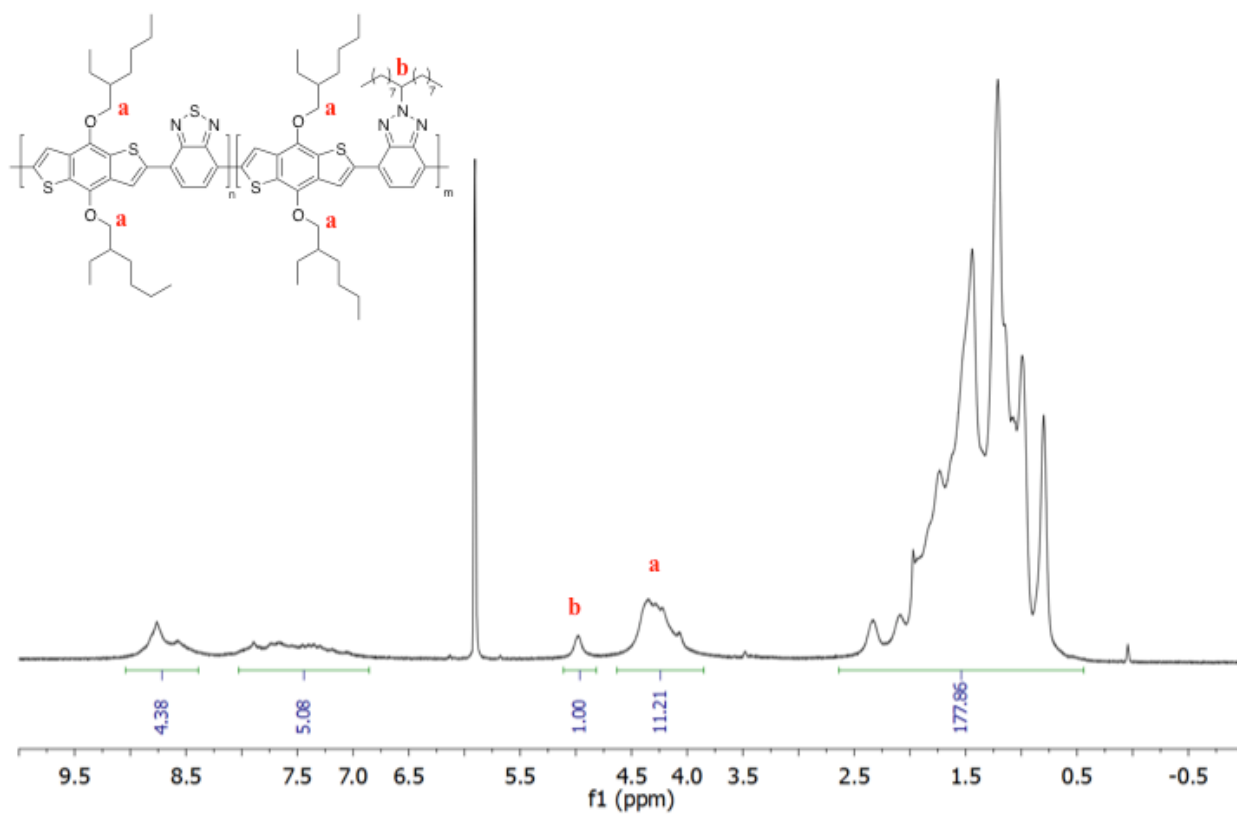


Figure S20. ^1H NMR spectrum of the polymer **P_{DA}2**

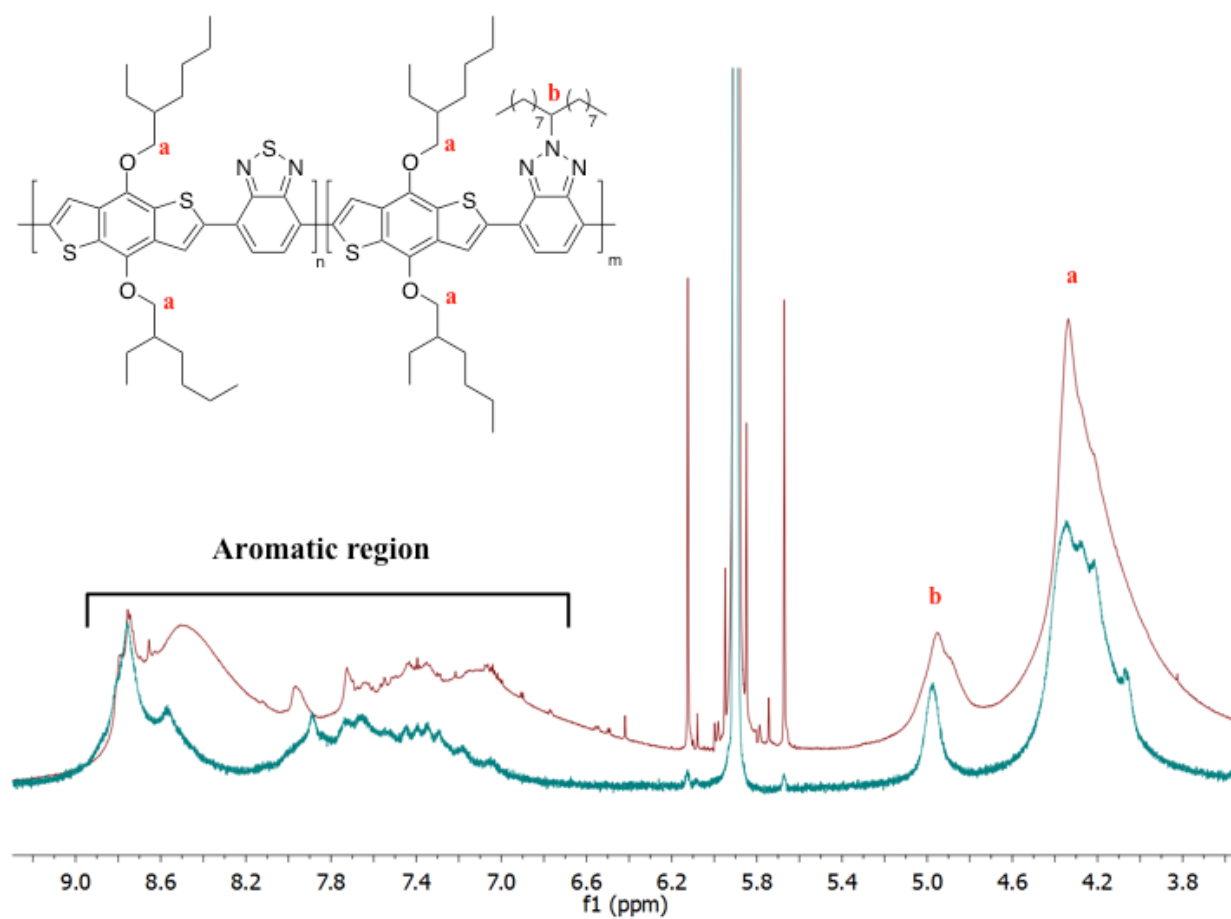
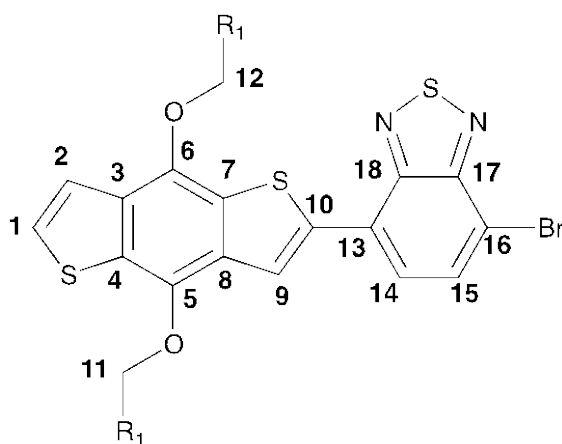


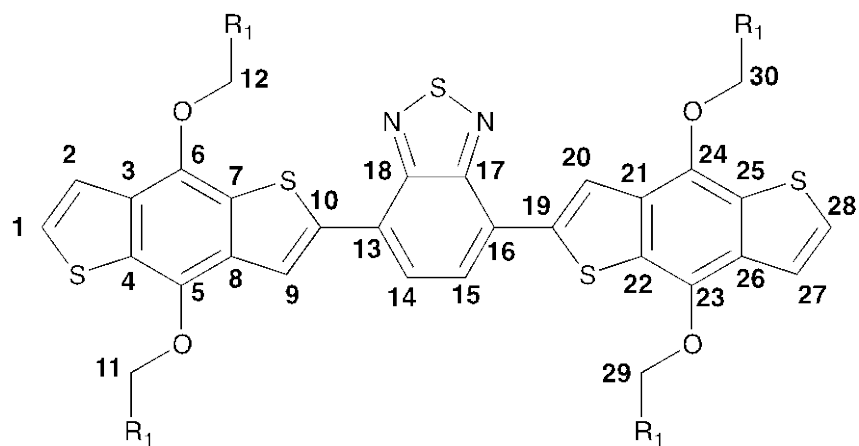
Figure S20a. High temperature ^1H NMR spectra of P_{DA2} and P_{STILLE} polymers (expansion of the region from 3.7 ppm to 9.5 ppm)

Table S2. ^1H and ^{13}C chemical shifts of **F2**. These tentative assignments were based on HSQC and HMBC experiments.



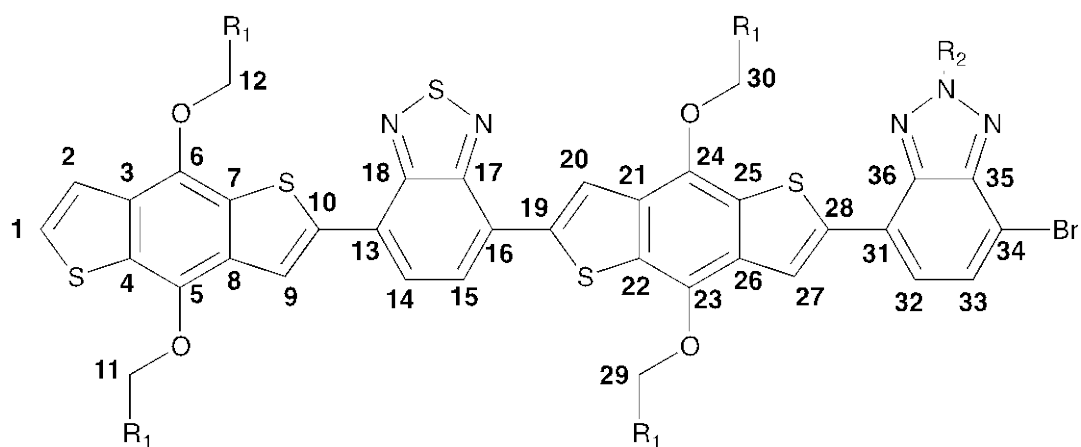
Position	$\delta(^{13}\text{C})$	$\delta(^1\text{H})$
1	126.5	7.41
2	120.3	7.48
3	130.3	---
4	132.5	---
5	145.3	---
6	144.1	---
7	132.2	---
8	128.8	---
9	122.8	8.78
10	137.4	---
11	76.2	4.27
12	76.1	4.21
13	127.0	---
14	127.2	7.76
15	132.1	7.89
16	113.3	---
17	153.8	---
18	151.8	---

Table S3. ^1H and ^{13}C chemical shifts of **F3**. These tentative assignments were based on HSQC and HMBC and NOESY experiments.



Position	$\delta(^{13}\text{C})$	$\delta(^1\text{H})$
1-28	126.5	7.38
2-27	120.4	7.47
3-26	130.2	---
4-25	132.4	---
5-24	145.3	---
6-23	144.1	---
7-22	132.4	---
8-21	128.9	---
9-20	122.5	8.85
10-19	138.2	---
11-30	76.2	4.29
12-29	76.0	4.23
13-16	126.4	---
14-15	127.0	7.94
17-18	152.7	---

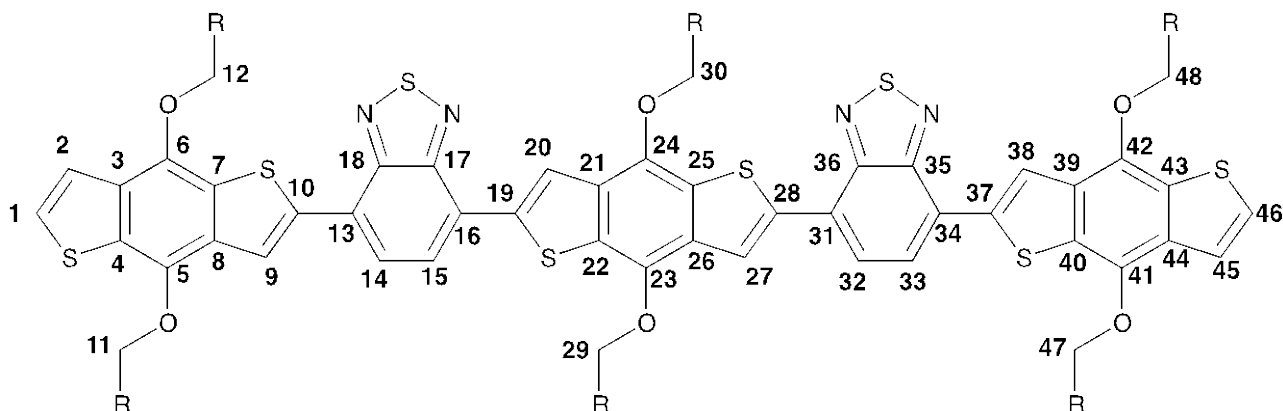
Table S4. ^1H and ^{13}C chemical shifts of **F4**. These tentative assignments were based on HSQC and HMBC and NOESY experiments.



Position	$\delta(^{13}\text{C})$	$\delta(^1\text{H})$
1	126.6	7.40
2	120.4	7.49
3	130.4	---
4	132.5	---
5	145.4	---
6	144.2	---
7	132.5 ₁	---
8	129.0	---
9	122.6	8.87
10	138.3	---
11	69.2-76.3	4.31
12		4.24
13	126.7	---
14	127.1-127.2	8.00
15	127.1-127.2	7.98
16	126.6	---
17	152.8	---
18	152.8	---
19	138.7	---

20	122.6	8.85
21	129.2-129.3	---
22	133.2	---
23	144.9	---
24	144.8	---
25	133.3	--
26	129.2-129.3	--
27	122.0	8.72
28	138.7	---
29	69.2-76.3	4.38
30		4.34
31	124.4	---
32	124.3	7.55
33	128.9	7.61
34	110.3	---
35	143.7	---
36	141.6	---

Table S5. ^1H and ^{13}C chemical shifts of **F5**. These tentative assignments were based on HSQC and HMBC and NOESY experiments.



Position	$\delta(^{13}\text{C})$	$\delta(^1\text{H})$
1-46	126.0	7.08
2-45	120.1	7.22
3-44	129.9	---
4-43	132.0	---
5-42	143.8	---
6-41	144.2	---
7-40	133.0	---
8-39	128.8	---
9-38	122.2	8.47
10-37	138.4	---
11-29-30-48	75.4-75.7	4.07-4.22
12-47	76.0	4.24
13-34	125.6	---
14-33	126.1-126.3	7.44
15-32	126.1-126.3	7.98
16-31	125.6	---
17-36	152.2	---
18-35	152.2	---
19-28	138.2	---
20-27	122.2	8.58

21-26	128.6	---
22-26	132.3	---
23-24	144.9	---

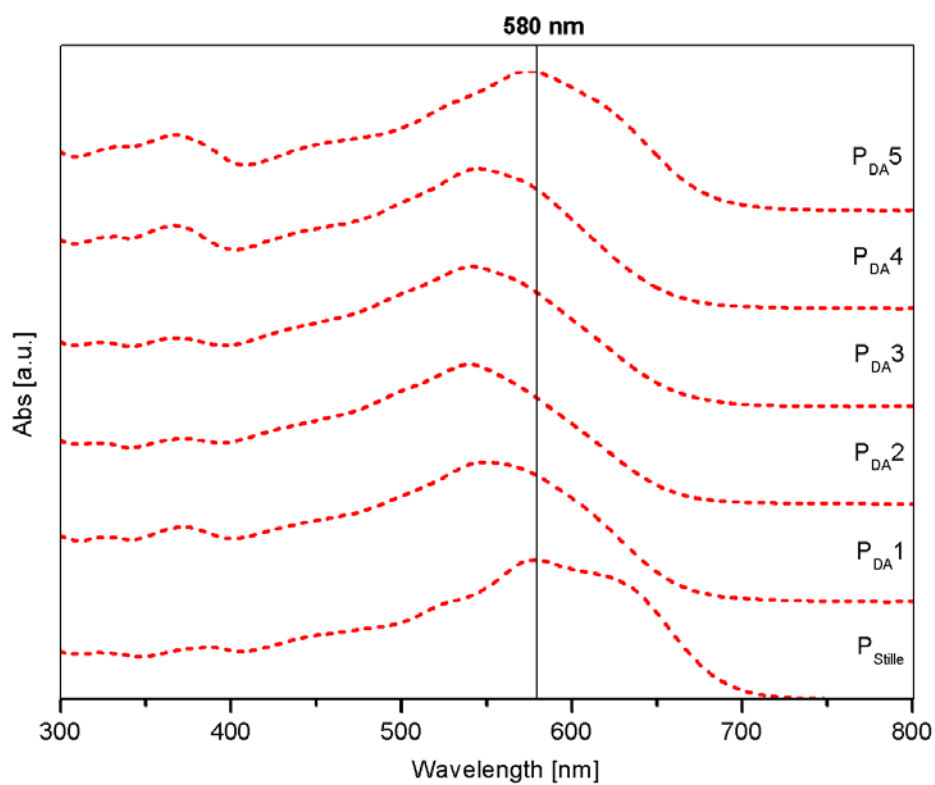


Figure S21. Normalized UV-Vis absorption spectra of the polymers **P_{DA}1-P_{DA}5** and **P_{Stille}** in chloroform solution.

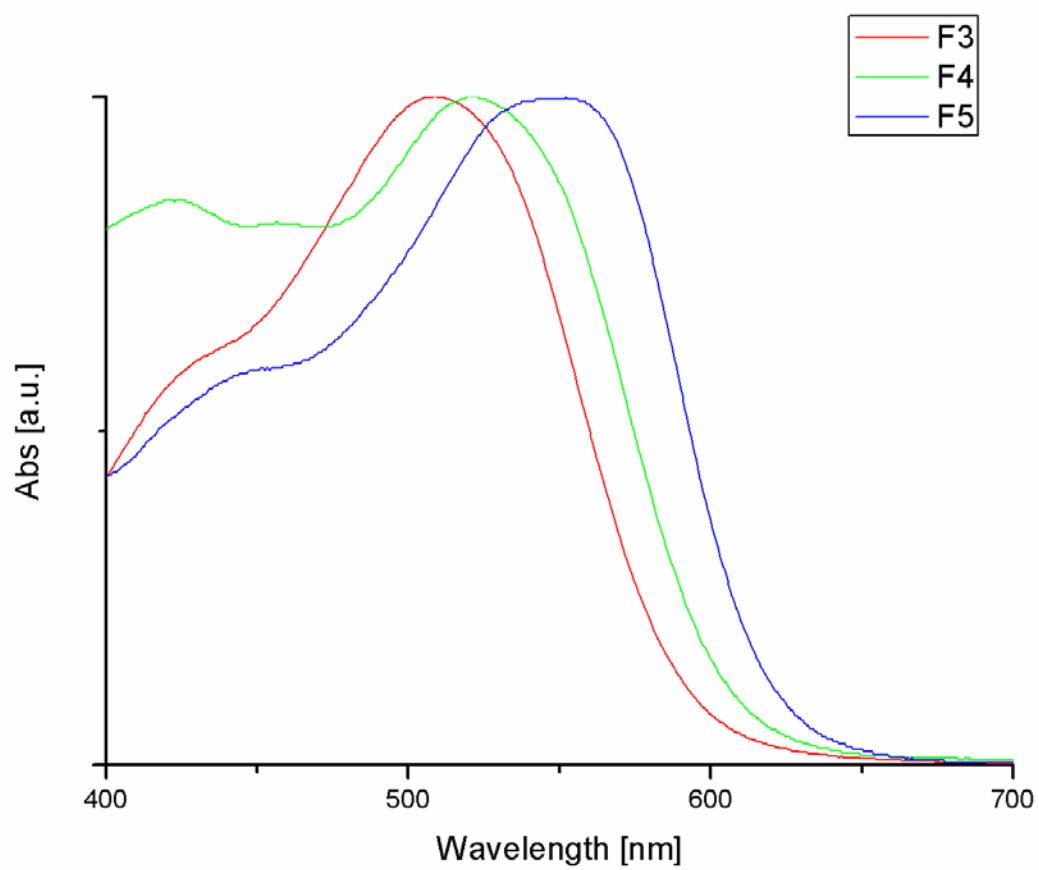


Figure S22. Normalized UV-Vis absorption spectra of the oligomers **F3-F5** in chloroform solution.

2. Device characterization

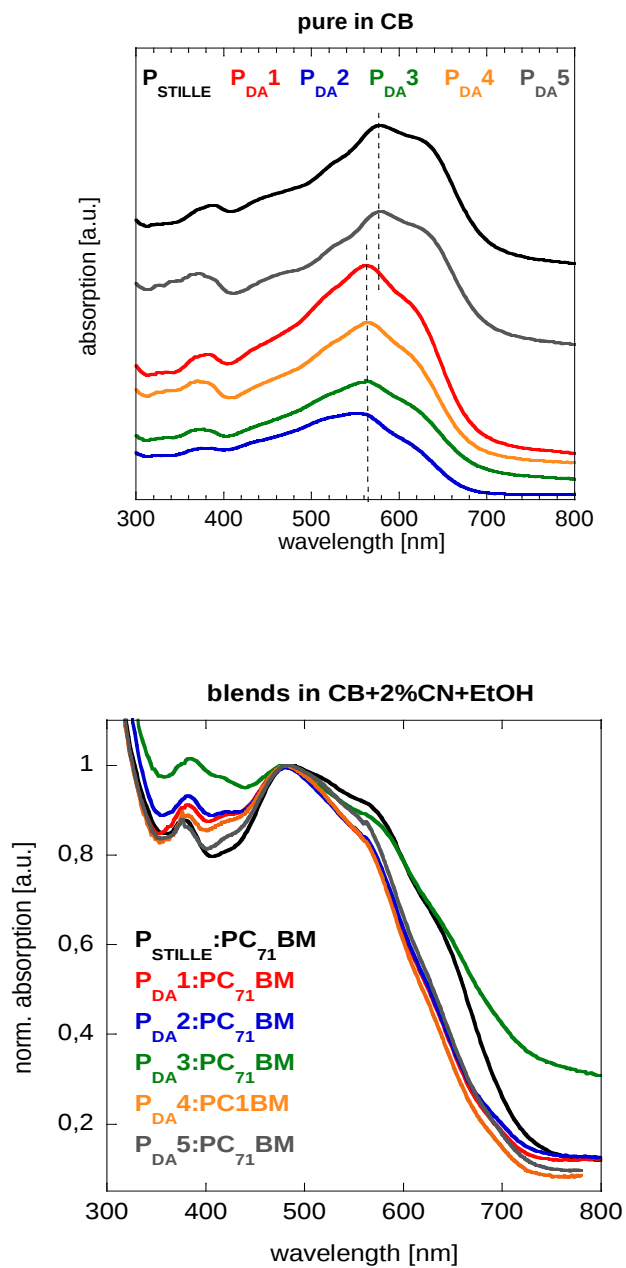


Figure S23. UV-Vis absorption spectra of pure P_{STILLE} and P_{DA} -s film polymers deposited from CB (top) and of $P_{STILLE}:PC_{71}BM$ and P_{DA} -s: $PC_{71}BM$ blend films deposited from CB+2%CN+EtOH (bottom).

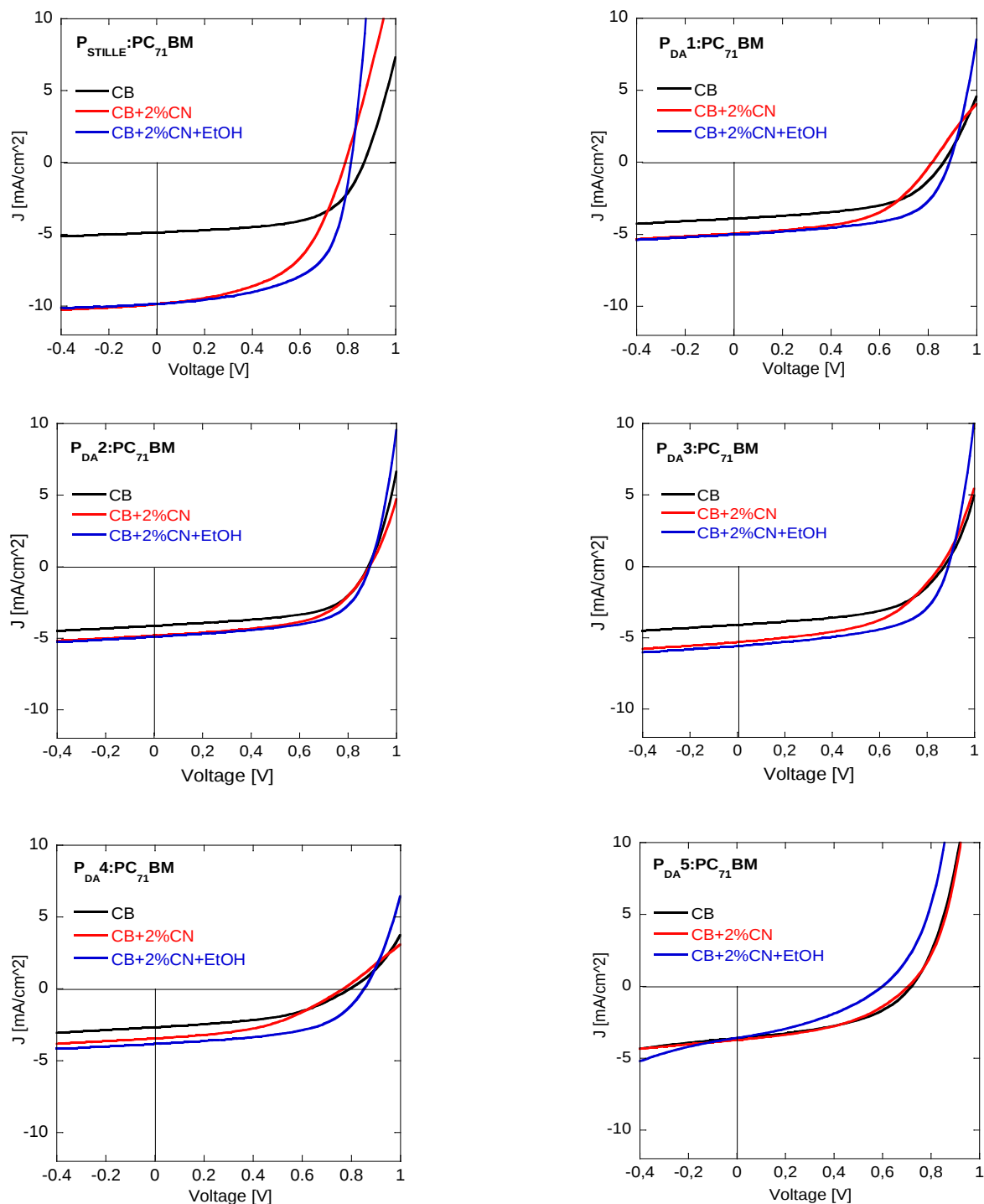


Figure S24. J-V characteristics of $P_{\text{STILLE}}:\text{PC}_{71}\text{BM}$ and $P_{\text{DA-s}}:\text{PC}_{71}\text{BM}$, 1:3 w:w, deposited from chlorobenzene (CB), CB with CN additive (CB+2%CN) and CB with CN additive + surface treatment with EtOH (CB+2%CN+EtOH), annealed 90°C for 5 min, cathode Al, under AM1.5G 100 mW/cm^2 solar simulation.

Table S6. Photovoltaic parameters of P_{STILLE}:PC₇₁BM and P_{DA-s}:PC₇₁BM solar cells, presented in Figure S27.

P _{STILLE} :PC ₇₁ BM	Voc [V]	FF [--]	Jsc [mA/cm ²]	PCE [%]
CB	0.87	0.60	4.88	2.54
CB+2%CN	0.79	0.52	9.88	4.06
CB+2%CN+EtOH	0.81	0.60	9.89	4.80
P _{DA1} :PC ₇₁ BM	Voc [V]	FF [--]	Jsc [mA/cm ²]	PCE [%]
CB	0.86	0.54	3.91	1.82
CB+2%CN	0.82	0.52	4.95	2.10
CB+2%CN+EtOH	0.89	0.59	5.02	2.60
P _{DA2} :PC ₇₁ BM	Voc [V]	FF [--]	Jsc [mA/cm ²]	PCE [%]
CB	0.88	0.58	4.13	2.11
CB+2%CN	0.89	0.55	4.80	2.37
CB+2%CN+EtOH	0.89	0.59	4.91	2.60
P _{DA3} :PC ₇₁ BM	Voc [V]	FF [--]	Jsc [mA/cm ²]	PCE [%]
CB	0.87	0.53	4.10	1.89
CB+2%CN	0.86	0.49	5.31	2.26
CB+2%CN+EtOH	0.89	0.56	5.58	2.80
P _{DA4} :PC ₇₁ BM	Voc [V]	FF [--]	Jsc [mA/cm ²]	PCE [%]
CB	0.79	0.46	2.68	0.98
CB+2%CN	0.77	0.44	3.46	1.16
CB+2%CN+EtOH	0.85	0.53	3.83	1.70
P _{DA5} :PC ₇₁ BM	Voc [V]	FF [--]	Jsc [mA/cm ²]	PCE [%]
CB	0.72	0.44	3.60	1.14
CB+2%CN	0.71	0.43	3.74	1.14
CB+2%CN+EtOH	0.60	0.36	3.59	0.80

Table S7. Photovoltaic parameters of the polymers **P_{DA1}**-**P_{DA5}** and **P_{STILLE}** upon CN processing and surface treatment with ethanol.

Polymer: PC ₇₁ BM(1:3)	V _{oc} [V]	FF [--]	J _{sc} [mA/cm ²]	PCE [%] ^a
P_{STILLE}	0.81	0.6	9.89	4.73 ± 0.08
P_{DA1}	0.89	0.59	5.02	2.55 ± 0.05
P_{DA2}	0.89	0.59	4.91	2.51 ± 0.06
P_{DA3}	0.89	0.56	5.58	2.72 ± 0.08
P_{DA4}	0.85	0.53	3.83	1.66 ± 0.04
P_{DA5}	0.6	0.36	3.59	0.74 ± 0.06

^a Average PCE obtained from 6 devices

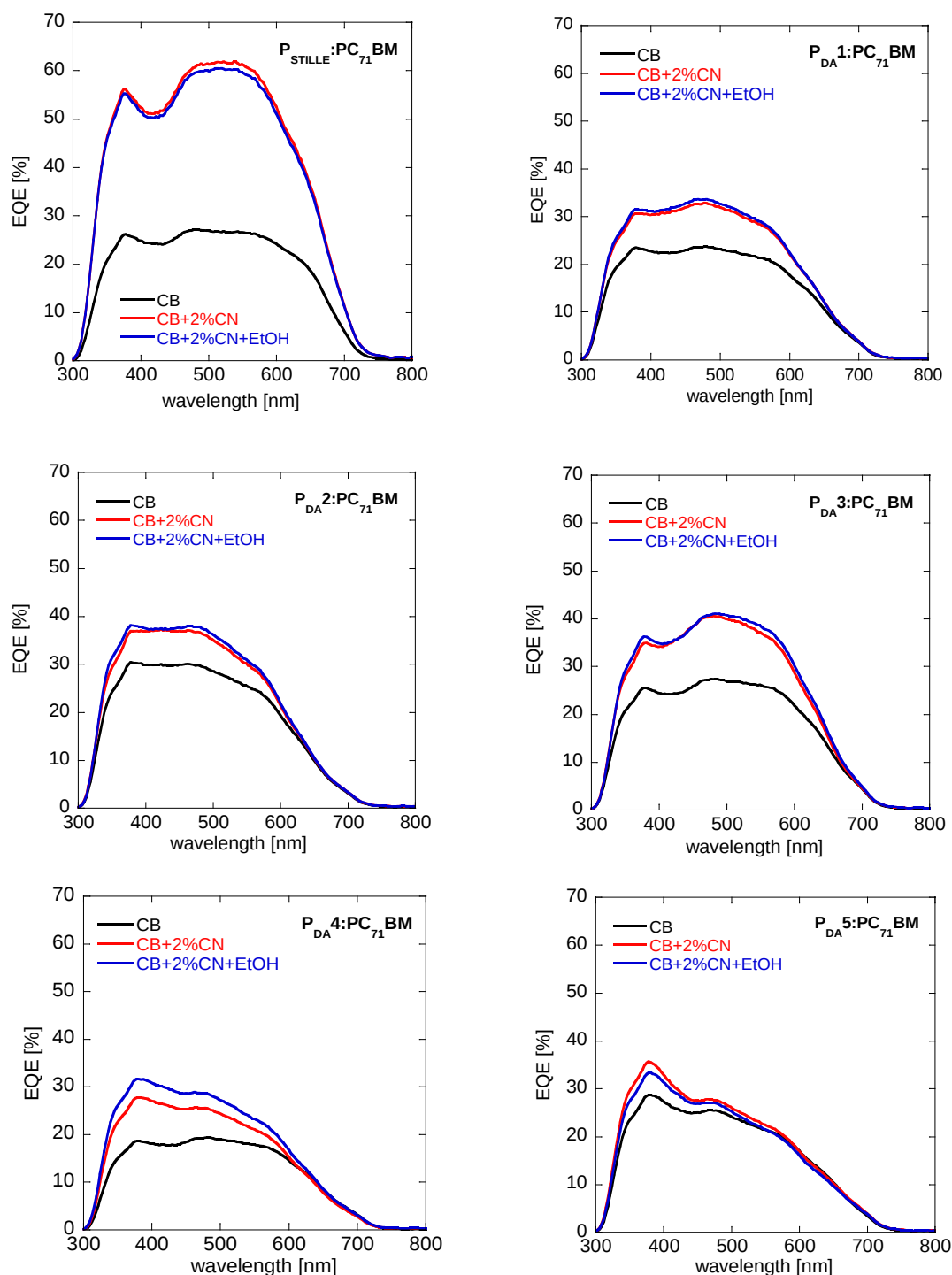


Figure S25 External Quantum Efficiency (EQE) of of P_{STILLE}: PC₇₁BM and P_{DA}-s:PC₇₁BM, 1:3 w:w, deposited from chlorobenzene (CB), CB with CN additive (CB+2%CN) and CB with CN additive + surface treatment with EtOH (CB+2%CN+EtOH), annealed 90°C for 5 min, cathode Al.

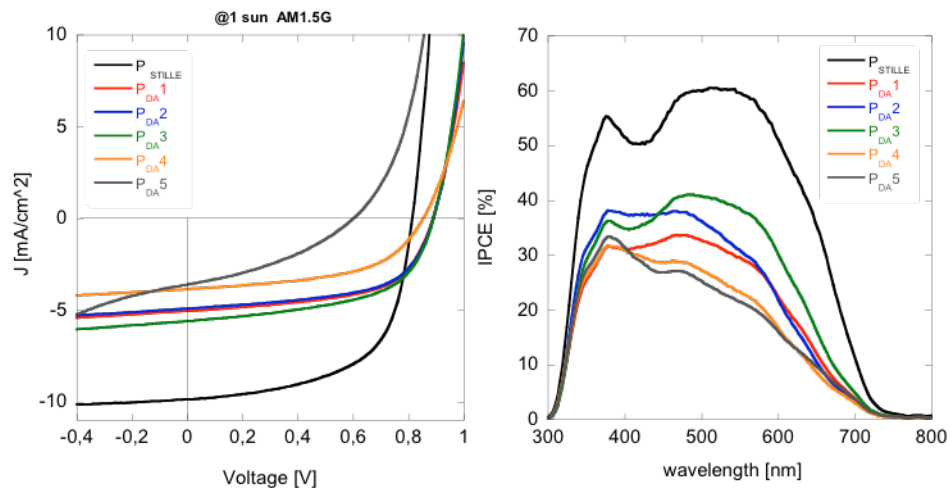


Figure S26. J-V (left) and EQE (right) characteristics of $P_{\text{DA-s:PC}_{71}\text{BM}}$, 1:3 from CB+2%CN + surface treatment with EtOH, annealed 90°C for 5 min, cathode Al, under AM1.5G 100 mW/cm^2 solar simulation.