Electronic Supplementary Information

Fluorination as an effective tool to increase the open-circuit voltage and charge carrier mobility of organic solar cells based on poly(cyclopenta[2,1-*b*:3,4-*b*']dithiophene-*alt*-quinoxaline) copolymers

Pieter Verstappen,[ab] *Jurgen Kesters,*[abc] *Wouter Vanormelingen,*[ab] *Gaël H. L. Heintges,*[ab] *Jeroen Drijkoningen,*[bc] *Tim Vangerven,*[bc] *Lidia Marin,*[ab] *Simplice Koudjina,*[d] *Benoît Champagne,*[d] *Jean Manca,*[bc] *Laurence Lutsen,*[b] *Dirk Vanderzande*[ab] *and Wouter Maes**[ab]

(a) Design & Synthesis of Organic Semiconductors (DSOS), Institute for Materials Research (IMO-IMOMEC), Hasselt University, Agoralaan 1 - Building D, B-3590 Diepenbeek, Belgium

(b) IMEC, IMOMEC, Universitaire Campus - Wetenschapspark 1, B-3590 Diepenbeek, Belgium

(c) Organic and Nanostructured Electronics & Energy (ONE^2), Institute for Materials Research (IMO-IMOMEC), Hasselt University, Universitaire Campus - Wetenschapspark 1, B-3590 Diepenbeek, Belgium

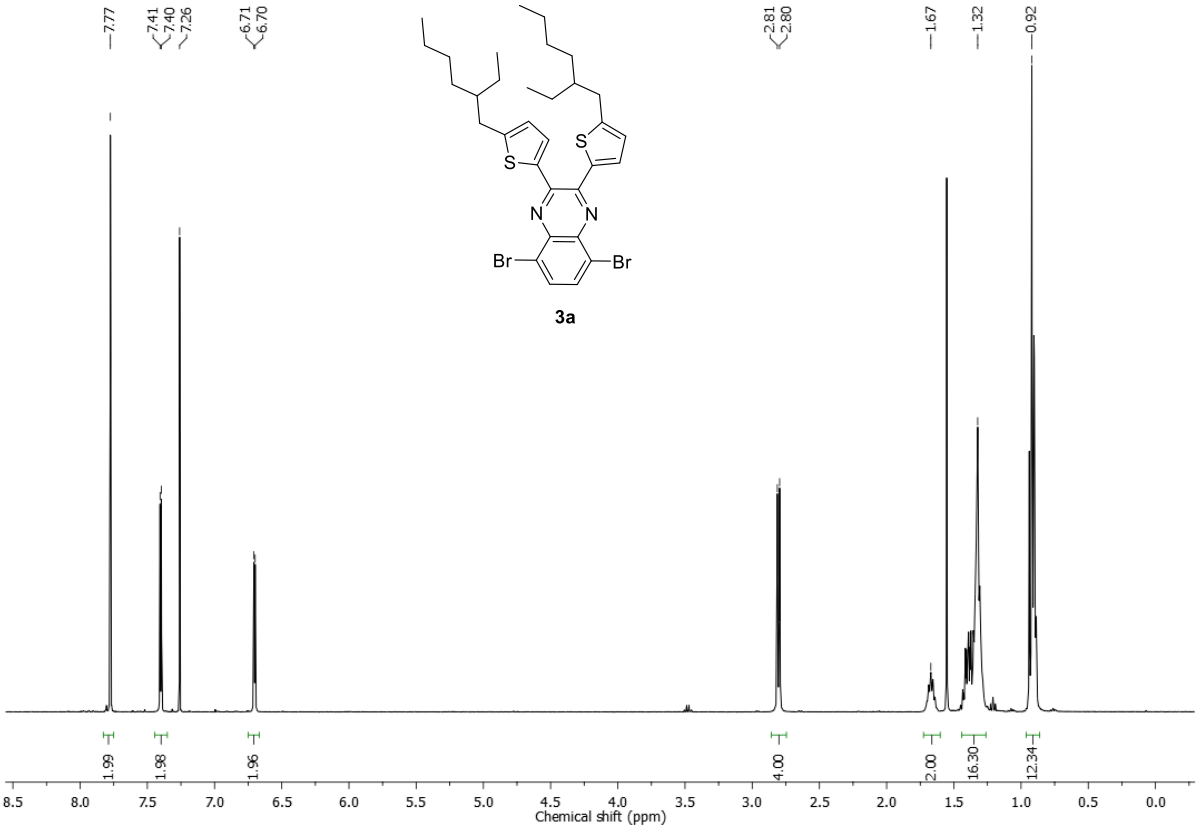
(d) Laboratoire de Chimie Théorique, University of Namur, Rue de Bruxelles 61, B-5000 Namur, Belgium

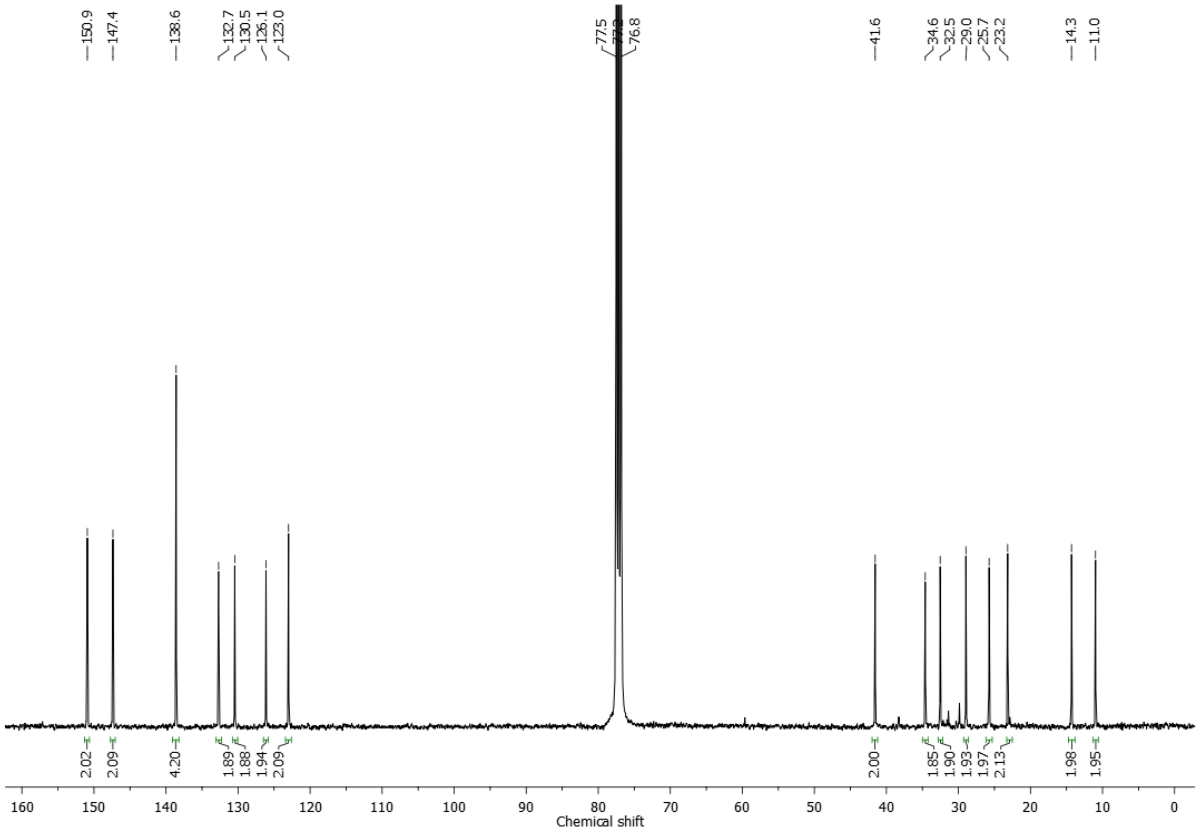
Corresponding author: Tel.: +32 11268312; Fax: +32 11268299; E-mail: wouter.maes@uhasselt.be

Table of contents

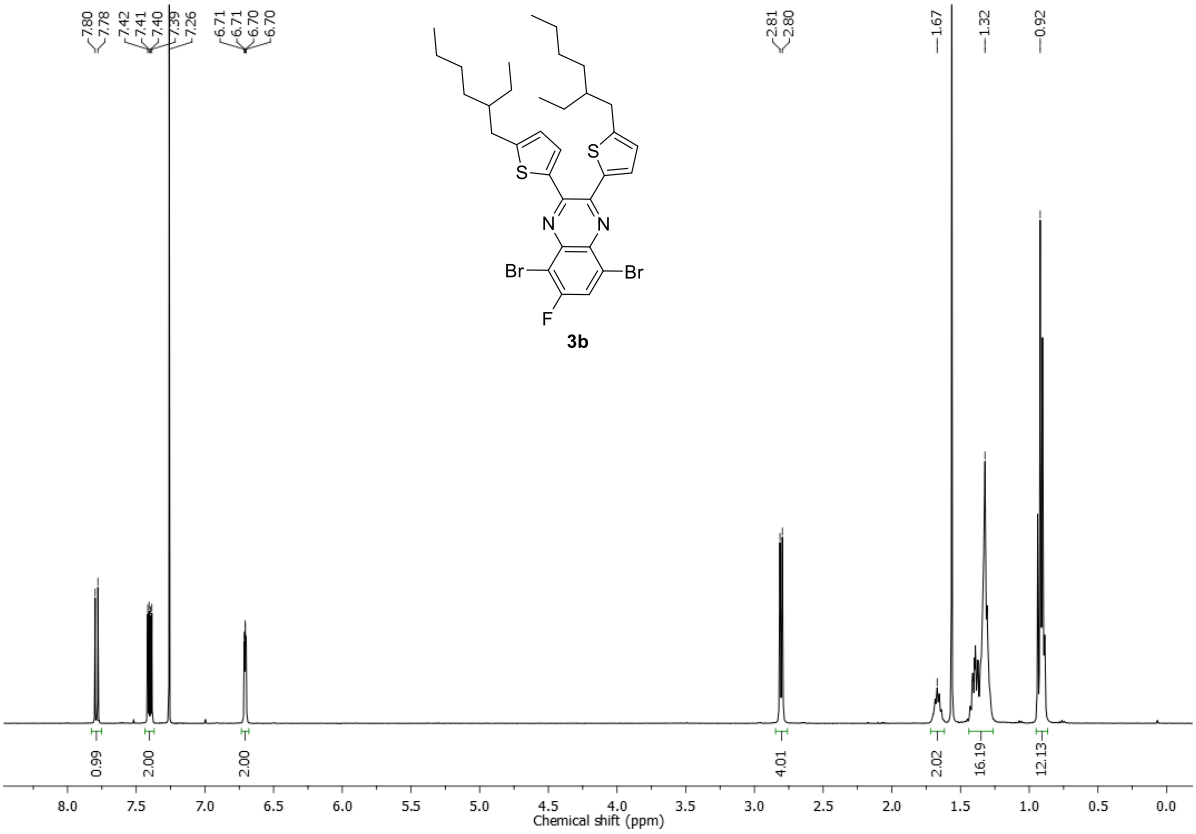
1. ^{1}H and ^{13}C NMR spectra

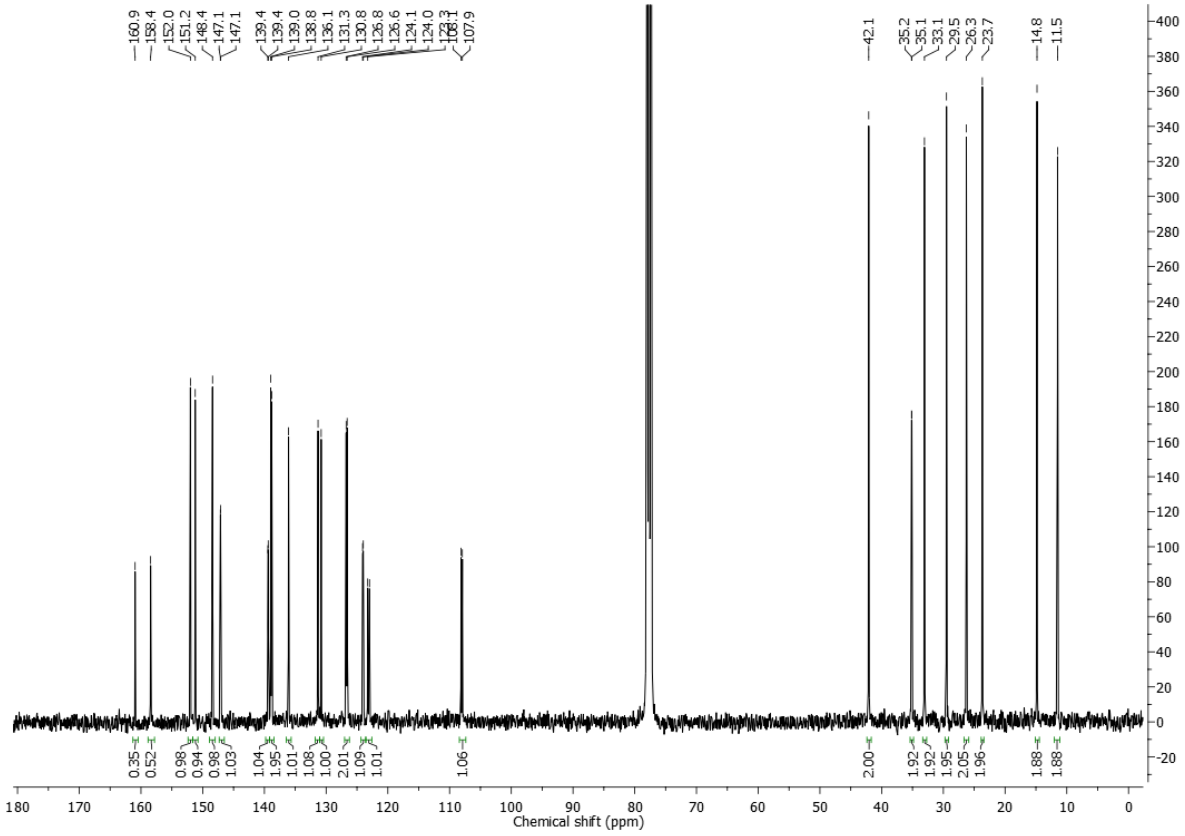
5,8-Dibromo-2,3-bis[5'-(2''-ethylhexyl)thiophen-2'-yl]quinoxaline (3a)



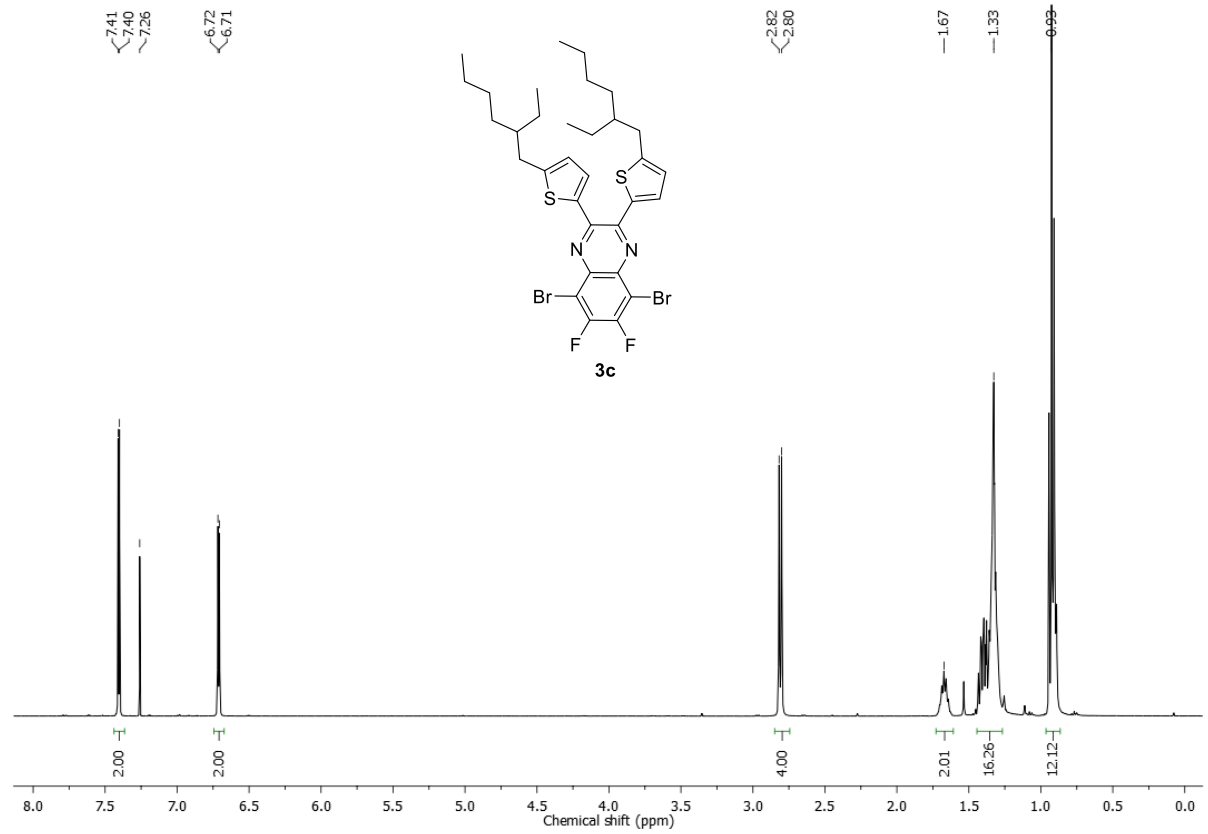


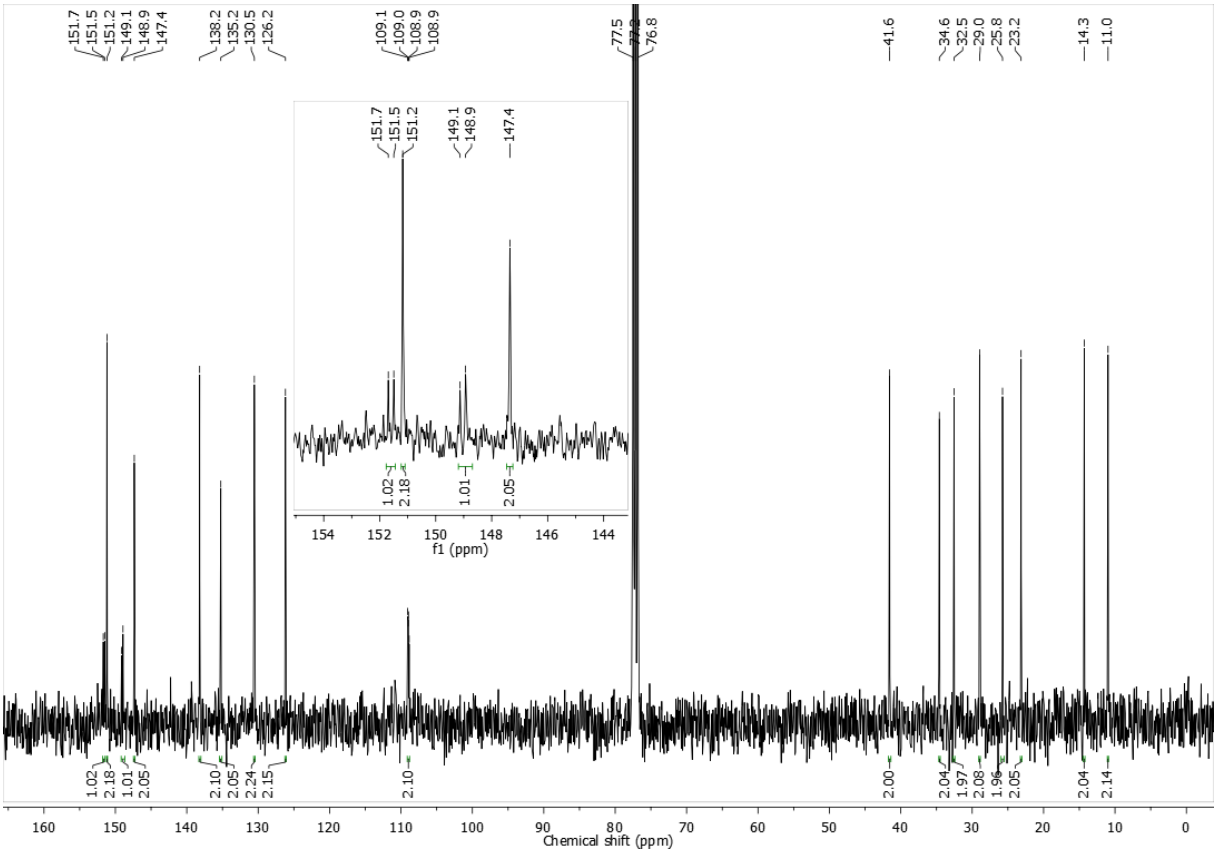
5,8-Dibromo-6-fluoro-2,3-bis[5'-(2''-ethylhexyl)thiophen-2'-yl]quinoxaline (3b)



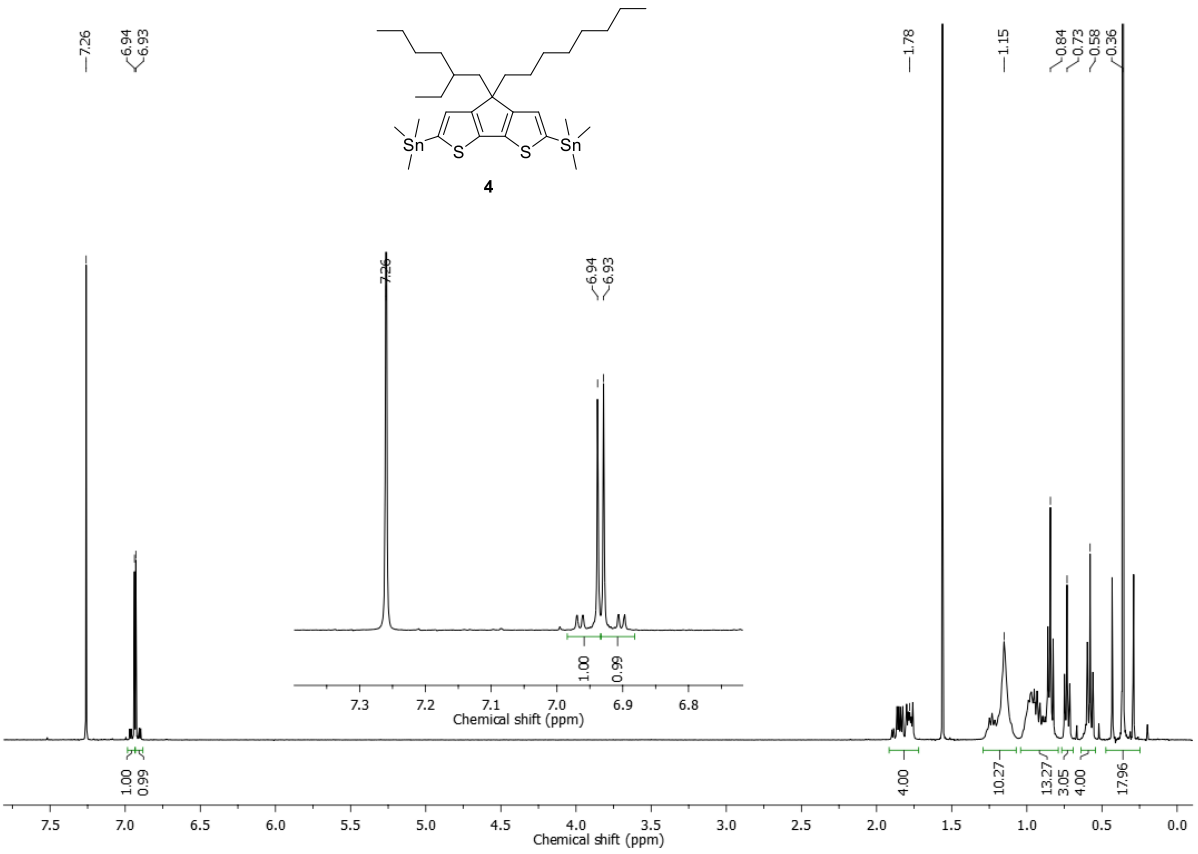


5,8-Dibromo-6,7-difluoro-2,3-bis[5'-(2''-ethylhexyl)thiophen-2'-yl]quinoxaline (3c)

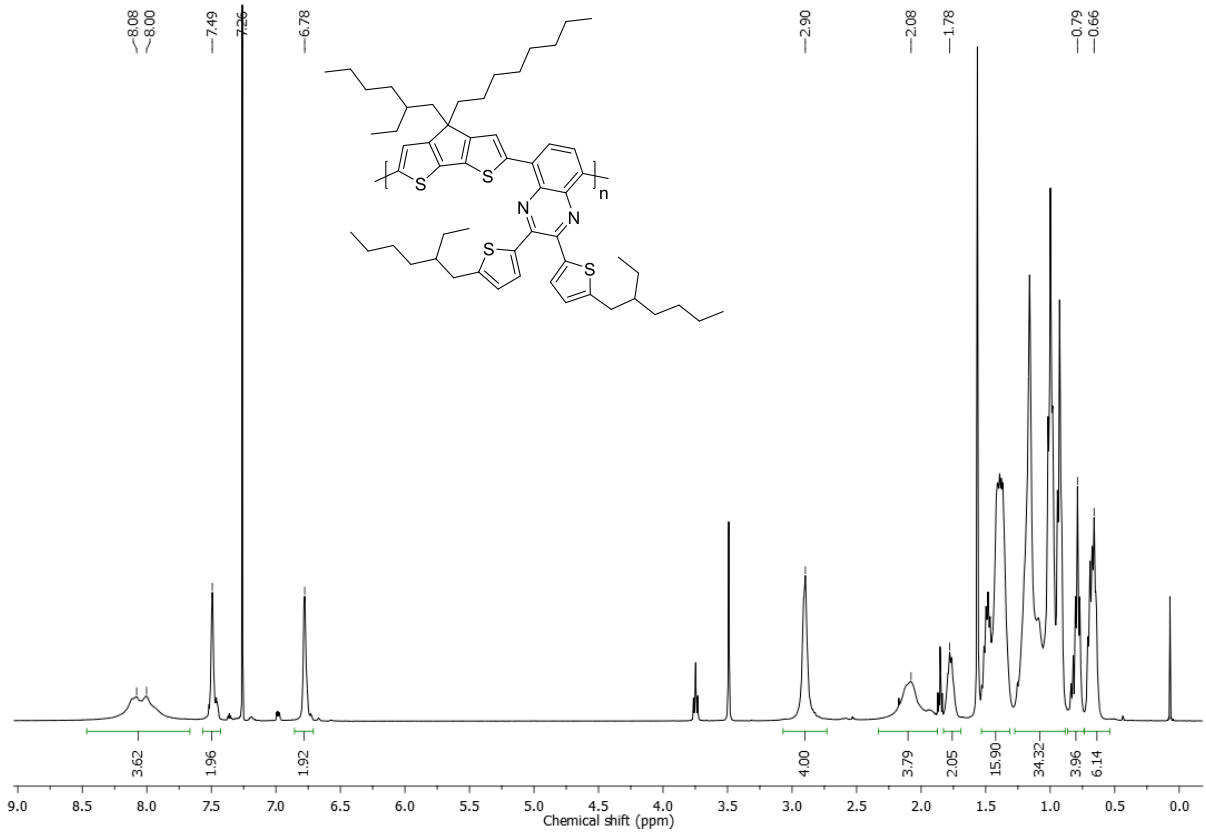




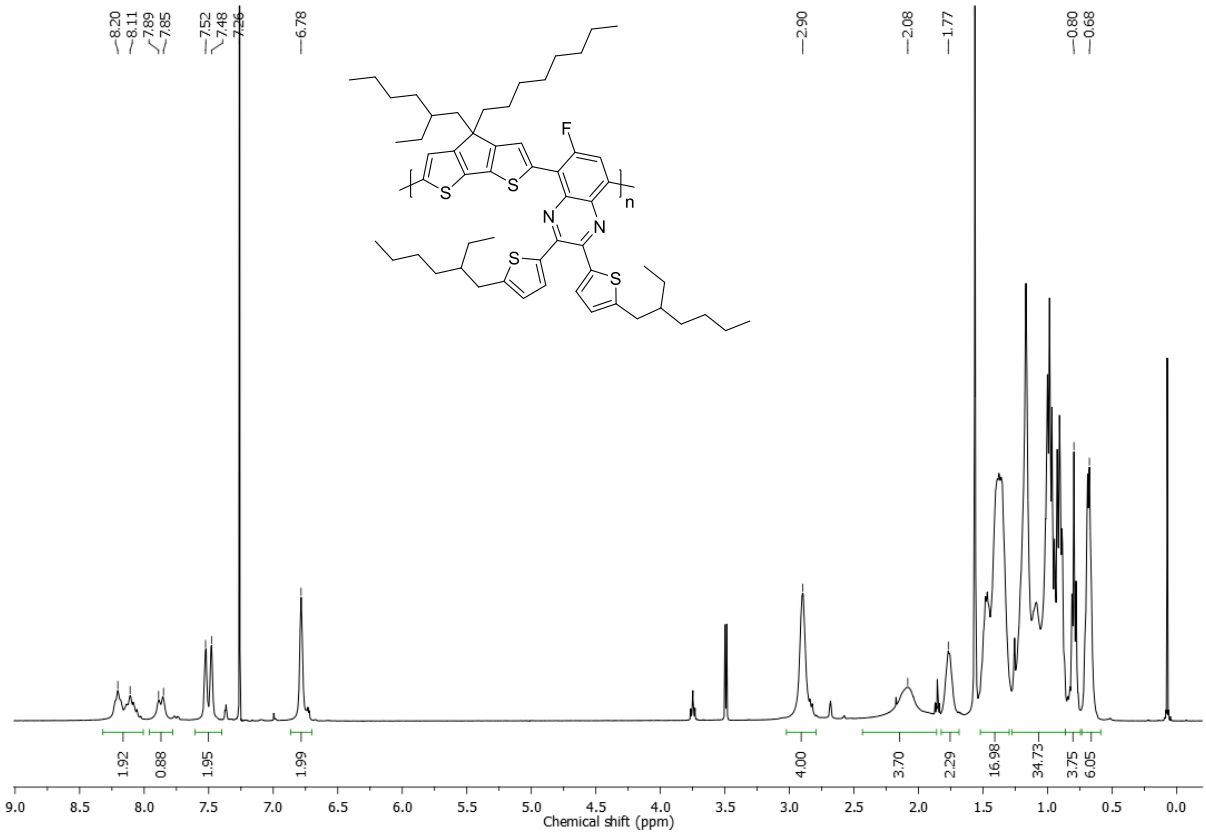
2,6-Bis(trimethylstannyl)-4-(2'-ethylhexyl)-4-octyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (4)



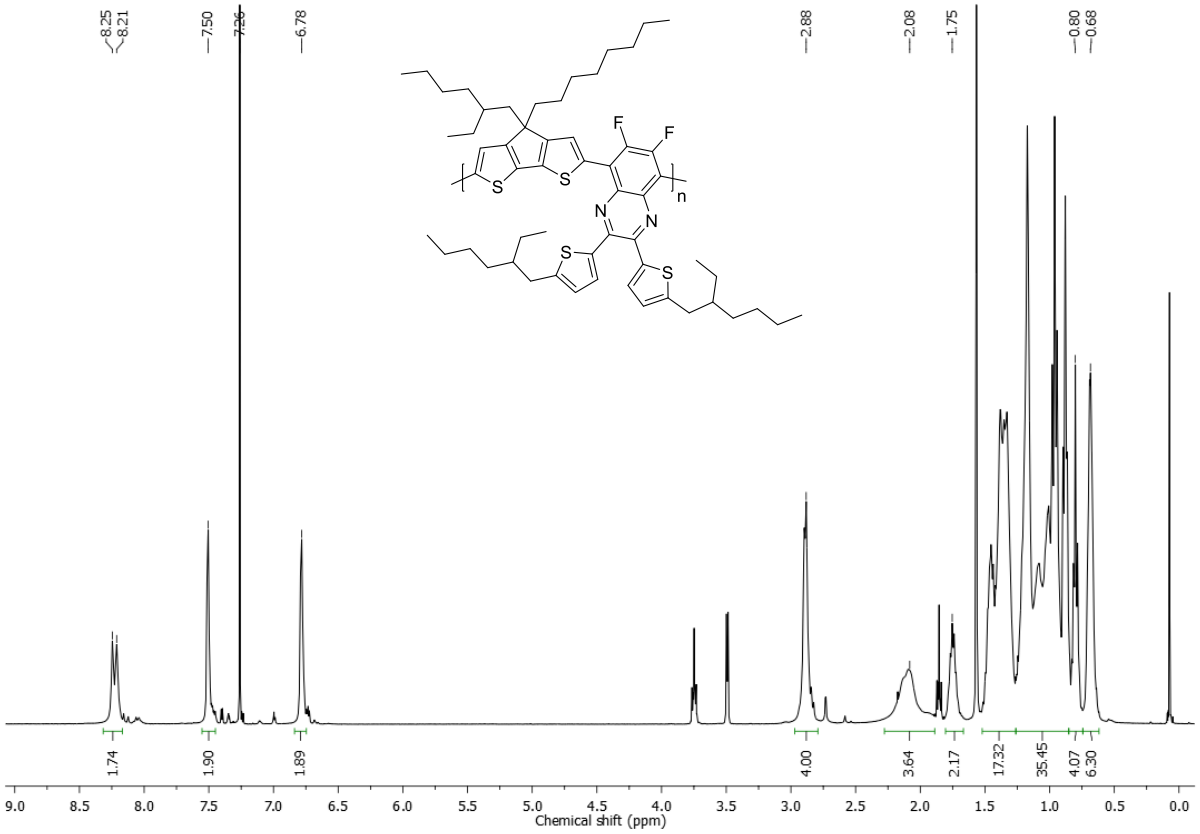
PCPDTQx(0F)



PCPDTQx(1F)



PCPDTQx(2F)


8.25
8.21
7.50
7.26
6.78
2.88
2.08
1.75
0.80
0.68
F
F
S
S
N
N
S
S
n
1.74
1.90
1.89
4.00
3.64
2.17
17.32
35.45
4.07
6.30
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical shift (ppm)

2. Optimization of the solar cell performance for each polymer

Table S1: Optimization of the solar cell devices based on **PCPDTQx(0F)**.

Processing solvent[a]	Polymer:$PC_{71}BM$	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	Average η (%)[b]	Best η (%)
CF	1:3[c]	0.61	6.55	0.53	2.11	2.26
CF + 10% ODCB	1:3	0.60	8.72	0.51	2.65	2.79
CF + 2% DIO	1:3	0.56	4.08	0.44	1.04	1.34
CB	1:3	0.62	6.47	0.49	1.97	2.30
CB + 3% DIO	1:3	0.60	4.73	0.46	1.32	1.45
CB + 3% CN	1:3	0.60	8.41	0.48	2.41	2.75
ODCB[d]	1:3	0.59	7.98	0.49	2.34	2.74
ODCB + 3% DIO[d]	1:3	0.59	4.35	0.45	1.18	1.51
ODCB + 3% CN[d]	1:3	0.60	8.46	0.53	2.70	2.94
ODCB[e]	1:3	0.60	8.63	0.51	2.65	2.88
ODCB + 3% CN[e]	1:3	0.60	9.44	0.54	3.08	3.24

[a] ODCB = *ortho*-dichlorobenzene, CF = chloroform, CB = chlorobenzene, CN = 1-chloronaphthalene, DIO = 1,8-diiodooctane. [b] Average values over at least 4 devices. [c] Optimal polymer:fullerene ratio found after device optimization for **PCPDTQx(1F)**. [d] Polymer concentration 8 mg/mL. [e] Polymer concentration 12 mg/mL.

Table S2: Optimization of the solar cell devices based on **PCPDTQx(1F)**.

Processing solvent[a]	Polymer:$PC_{71}BM$	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	Average η (%)[b]	Best η (%)
CF	1:3[c]	0.72	7.21	0.52	2.71	3.10
CF + 10% ODCB	1:3	0.71	11.17	0.58	4.56	4.87
CF + 2% DIO	1:3	0.70	3.17	0.46	1.00	1.12
CB	1:3	0.69	6.79	0.47	2.20	2.46
CB + 2% DIO	1:3	0.68	4.16	0.46	1.29	1.62
CB + 3% CN	1:3	0.68	10.85	0.53	3.91	4.47
ODCB[d]	1:3	0.64	8.34	0.48	2.58	2.79
ODCB + 3% DIO[d]	1:3	0.65	2.75	0.42	0.75	0.96
ODCB + 3% CN[d]	1:3	0.61	9.47	0.44	2.50	2.72

[a] ODCB = *ortho*-dichlorobenzene, CF = chloroform, CB = chlorobenzene, CN = 1-chloronaphthalene, DIO = 1,8-diiodooctane. [b] Average values over at least 4 devices. [c] Optimal polymer:fullerene ratio found after device optimization for **PCPDTQx(1F)**. [d] Polymer concentration 8 mg/mL.

Table S3: Optimization of the solar cell devices based on **PCPDTQx(2F)**.

Processing solvent[a]	Polymer:$PC_{71}BM$	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	Average η (%)[b]	Best η (%)
CF	1:3[c]	0.73	5.63	0.48	1.98	2.42
CF + 10% ODCB	1:3	0.81	8.46	0.53	3.63	3.78
CF + 3% CN	1:3	0.82	7.92	0.57	3.65	4.07
CB	1:3	0.78	5.55	0.53	2.28	2.49
CB + 3% CN	1:2.5	0.83	10.39	0.56	4.86	5.26
CB + 3% CN	1:3	0.82	8.56	0.56	3.91	4.48
CB + 3% CN	1:3.5	0.80	8.15	0.55	3.57	3.72
ODCB[d]	1:3	0.80	8.11	0.48	3.12[e]	3.12

[a] ODCB = *ortho*-dichlorobenzene, CF = chloroform, CB = chlorobenzene, CN = 1-chloronaphthalene. [b] Average values over at least 4 devices. [c] Optimal polymer:fullerene ratio found after device optimization for **PCPDTQx(1F)**. [d] Polymer concentration 8 mg/mL. [e] Only one device was made.

3. Thermal analysis

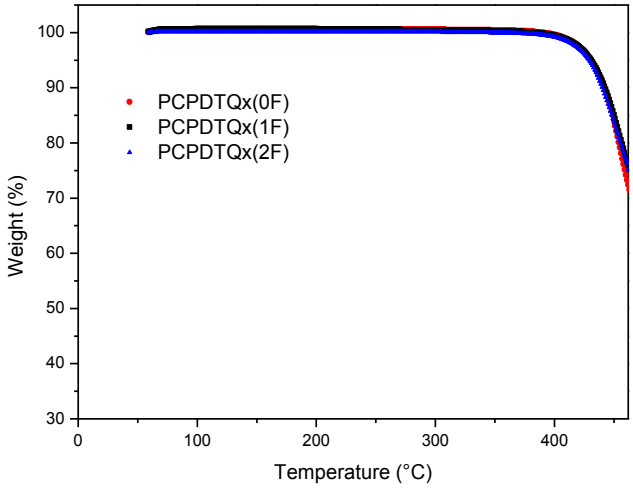


Figure S1: TGA profiles for the three PCPDTQx copolymers.

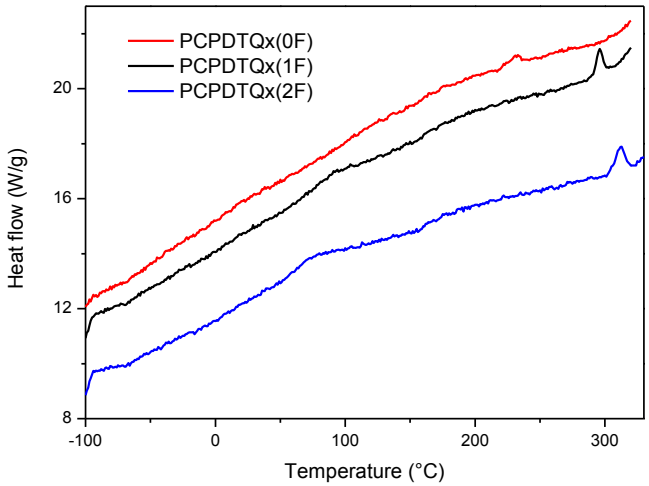


Figure S2: RHC profiles for the three PCPDTQx copolymers.

4. Photo-CELIV

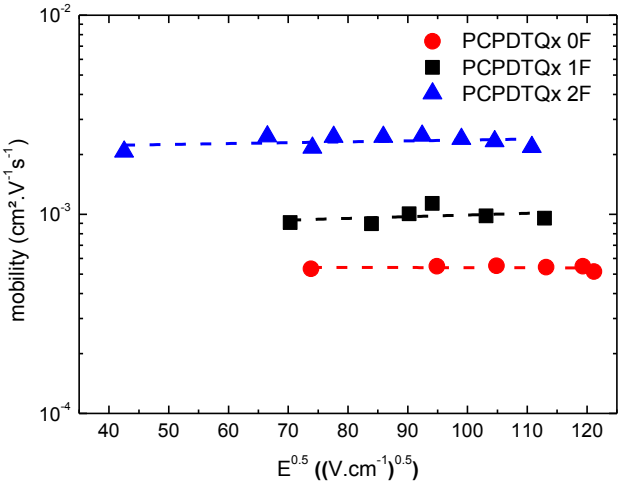


Figure S3: Photo-CELIV measurements on photovoltaic devices for the three PCPDTQx copolymers.

5. DMT modulus measurements

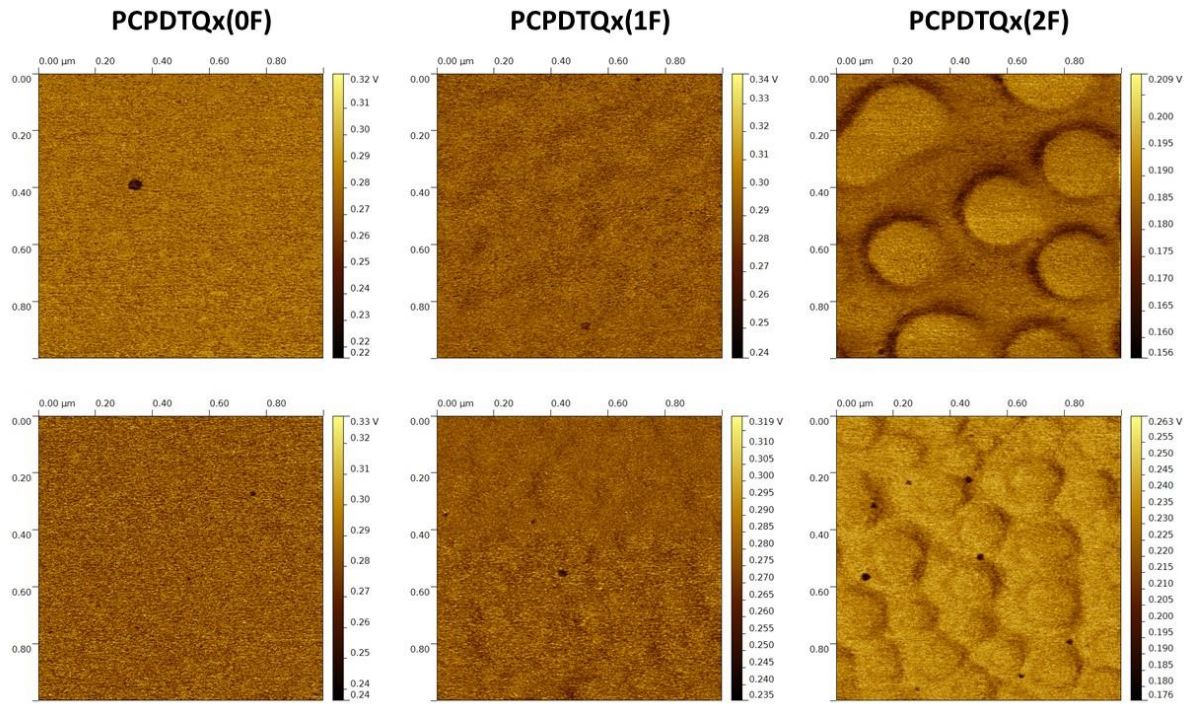


Figure S4: DMT modulus images of the photoactive layers of the PCPDTQx:$PC_{71}BM$ solar cells prepared without (upper row) and with (bottom row) processing additives.