Electronic Supplementary Information

Structural Variation of Donor-Acceptor Copolymers Containing Benzodithiophene with Bithienyl Substituents to Achieve High Open Circuit Voltage in Bulk Heterojunction Solar Cells

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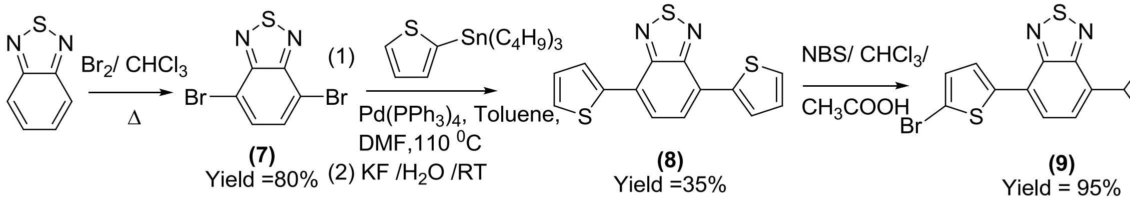


Scheme S 1. Synthesis of 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole.

The monomers 7 to 9 were synthesized from previously reported procedures with slight modifications in some steps.[1, 2]

*Synthesis of 4,7-dibromobenzo[c][1,2,5]thiadiazole (**7**)*

Benzo[*c*][1,2,5]thiadiazole (4.0 g, 0.029 mol) was dissolved in chloroform (30 mL). Bromine (21.93 mL, 0.440 mol) was added to the reaction flask and the reaction was stirred for 2 days at 60 °C in dark. The reaction mixture was cooled to room temperature and was quenched in solution of NaOH (4 M). The organic phase was extracted into chloroform and was washed with brine (3 × 100 mL), water (3 × 100 mL), and dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuum to obtain a white solid which was further purified by column chromatography using hexanes as the eluent to obtain 6.82 g of white needle like crystals (0.0232 mol, 80%). ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.72 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 113.9, 132.3, 152.9.

*Synthesis 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**8**)*

4,7-Dibromobenzo[*c*][1,2,5]thiadiazole (1.5 g, 0.00510 mol), 2-(tributylstannyl)thiophene (3.40 mL, 0.0107 mol) , and tetrakis(triphenylphosphine)palladium(0) (203 mg, 2.0×10^{-4} mol) were added to a three neck flask under a nitrogen atmosphere followed by the addition of toluene (25 mL) and DMF (0.5 mL). The reaction mixture was refluxed for 12 hrs at which time a sample was taken to determine the monomer conversion. When there was no starting material in the reaction mixture the reaction was cooled and potassium fluoride (6 g) in water (10 mL) was added to the reaction mixture and was stirred for 2 hours. The reaction mixture was quenched in ice cold water (100 mL). And the organic phase was extracted into methylene chloride (3 × 100 mL). The organic phase was washed with 10% hydrochloric acid (3 × 100 mL), with saturated $NaHCO_3$ (3 × 100 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuum to obtain a red solid, which was further purified by column chromatography using 99:1 hexanes: ethyl acetate as the eluent to obtain 0.535 g of red needle like crystals (0.00178 mol, 35%). ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.21 (t, 2H), 7.46 (d, 2H), 7.87 (s, 2H), 8.12 (d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 125.8, 126.0, 126.8, 127.5, 128.0, 139.3, 152.6.

*Synthesis of 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5] thiadiazole (**9**)*

4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (0.160 g, 5.0×10^{-4} mol) was dissolved in a mixture of chloroform (20 mL) and acetic acid (20 mL). At 0 °C NBS (0.208 g, 0.00117 mol) was added slowly to the reaction mixture. After 1 hour a red color compound precipitated, at this time the reaction was quenched in water (100 mL) and the organic phase was extracted into chloroform (3 × 100 mL). The organic phase was washed with water (3 × 100 mL) dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuum to obtain a 0.206 g of red solid (4.5×10^{-4} mol, 90%). ^1H NMR (500 MHz, Toluene-

d_8): δ_H 6.84 (d, 2H), 7.18 (s, 2H), 7.56 (d, 2H). ^{13}C NMR (125 MHz, Toluene-d_8): δ_C 115.0, 125.1, 125.9, 127.9, 131.1, 141.5, 152.7.

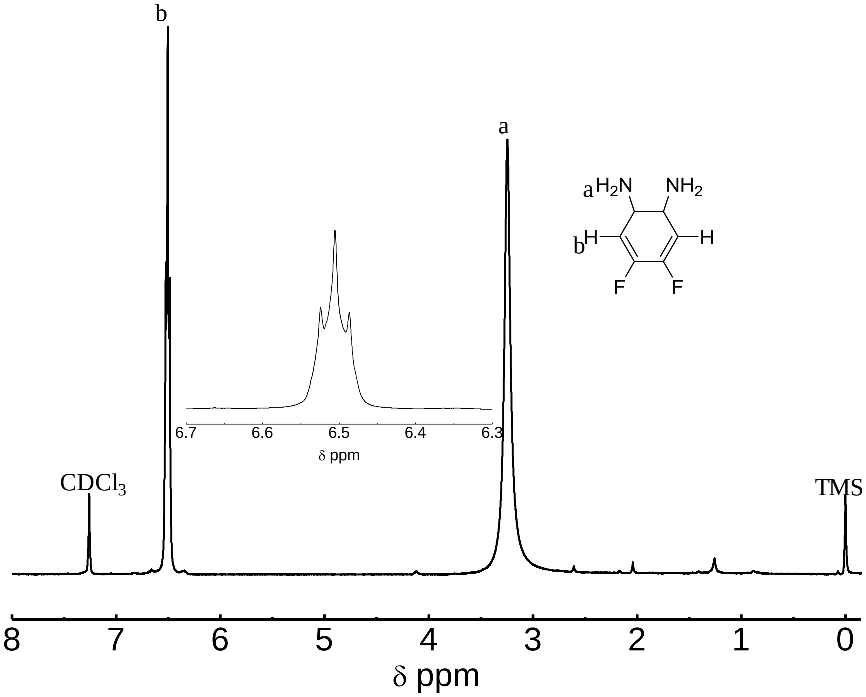


Fig. S 1 ^{1}H NMR spectrum of 4,5-difluorobenzene-1,2-diamine (1)

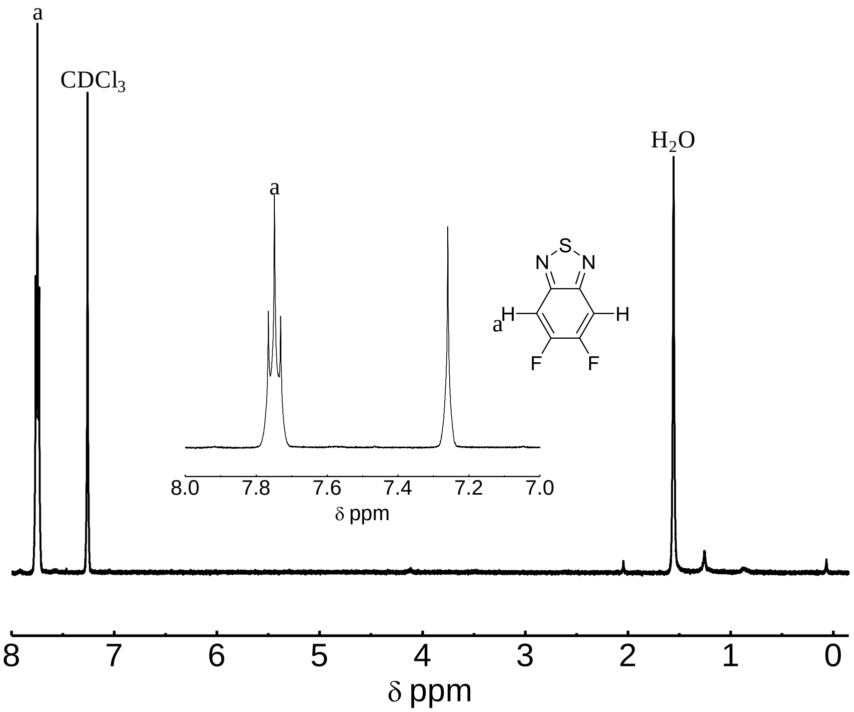


Fig. S 2 ^{1}H NMR spectrum of 5,6-difluorobenzo[*c*][1,2,5]thiadiazole (2)

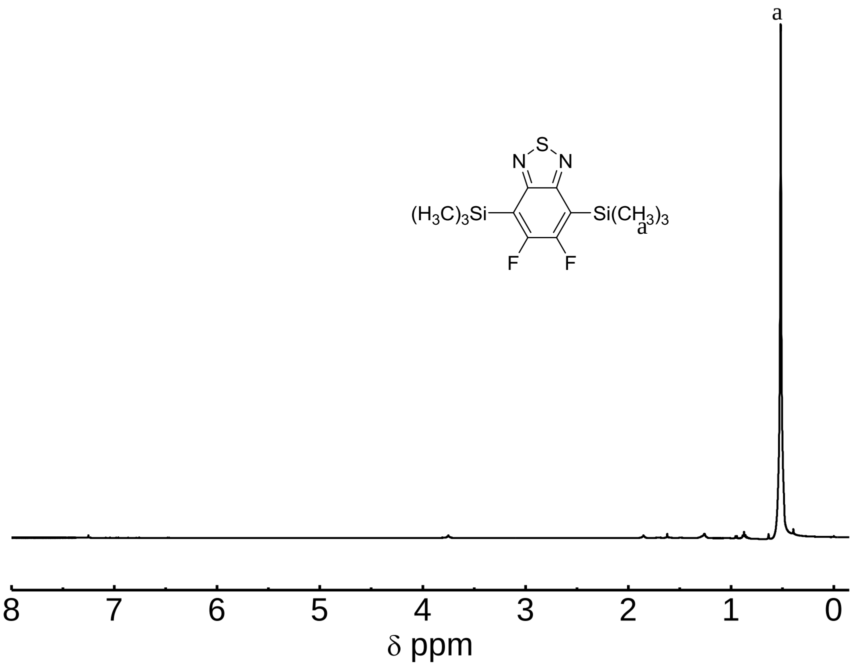


Fig. S 3 ^{1}H NMR spectrum of 5,6-difluoro-4,7-bis(trimethylsilyl)benzo[*c*][1,2,5] thiadiazole (3)

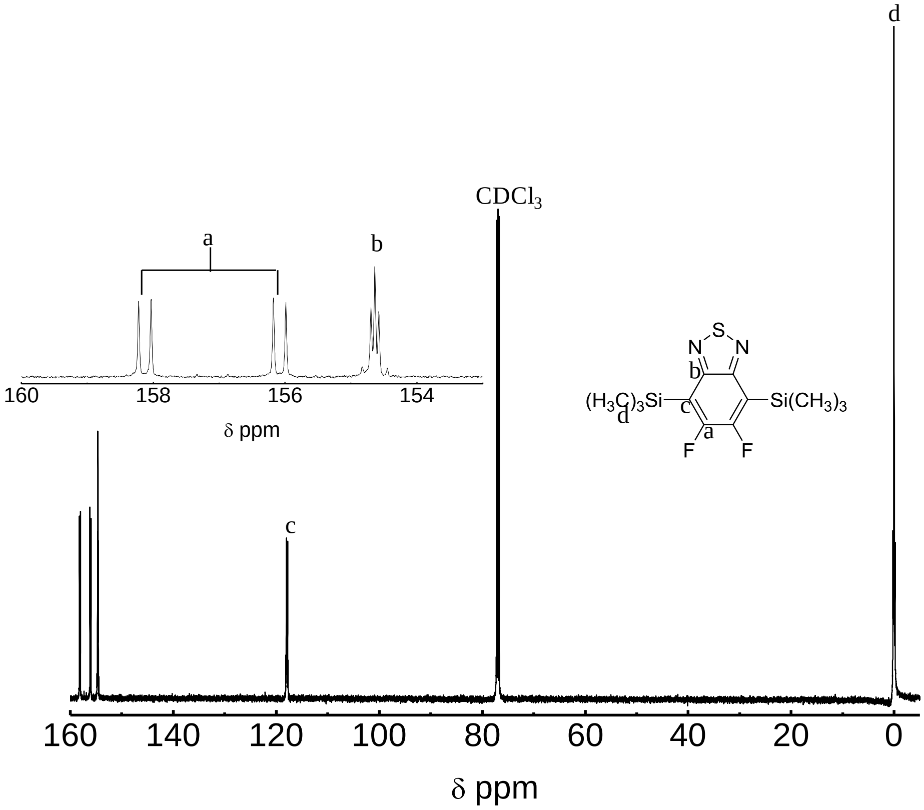


Fig. S 4 ^{13}C NMR spectrum of 5,6-difluoro-4,7-bis(trimethylsilyl)benzo[*c*][1,2,5]thiadiazole (3)

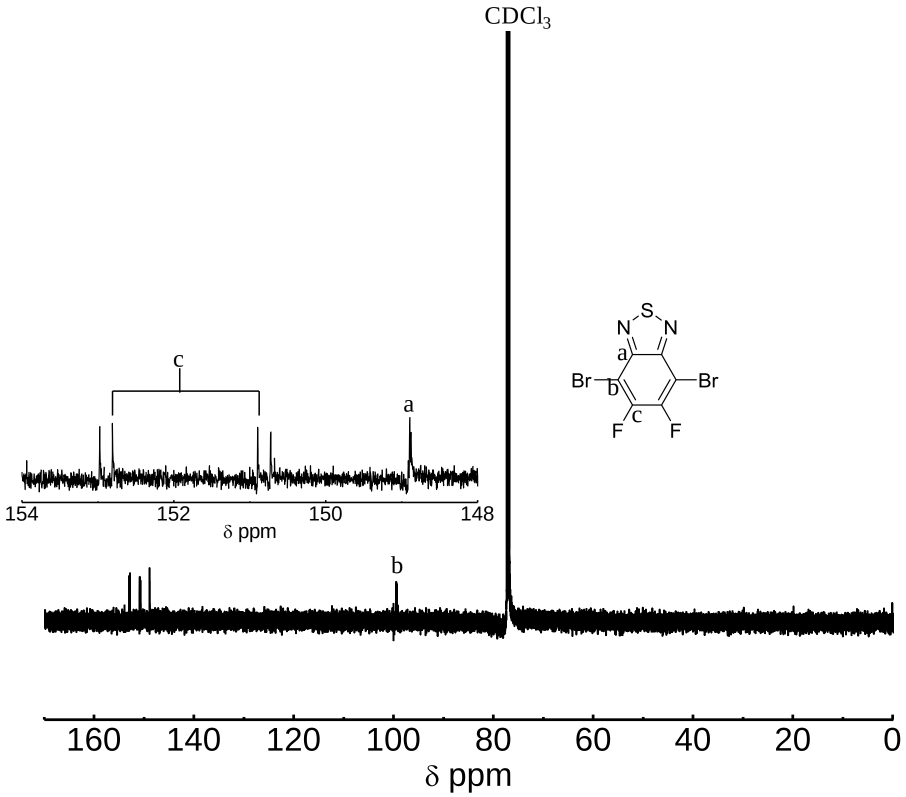


Fig. S 5 ^{13}C NMR spectrum of 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (4)

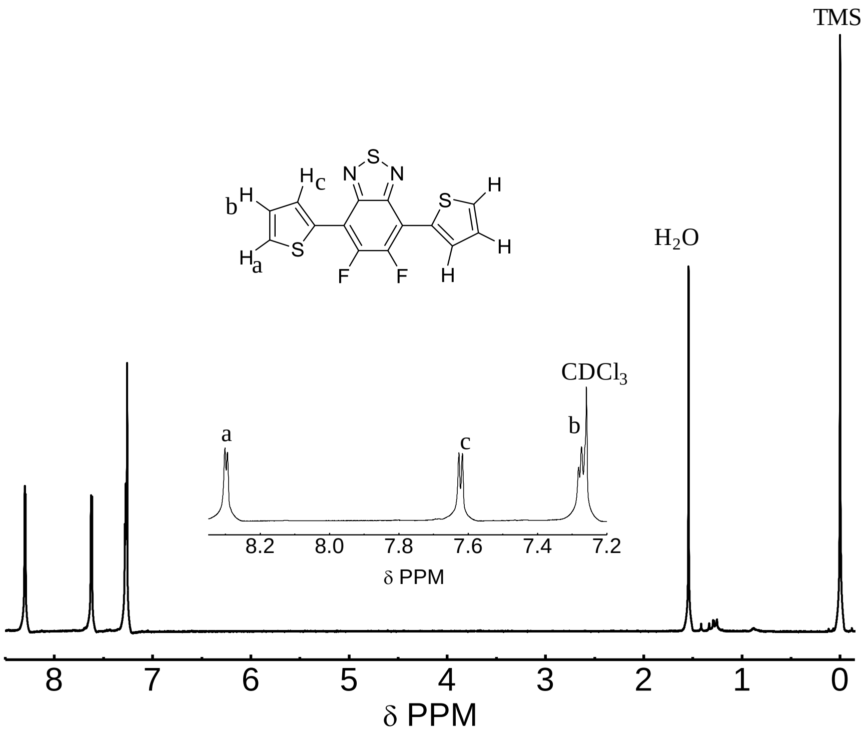


Fig. S 6 ^{1}H NMR spectrum of 5,6-difluoro-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5] thiadiazole (5)

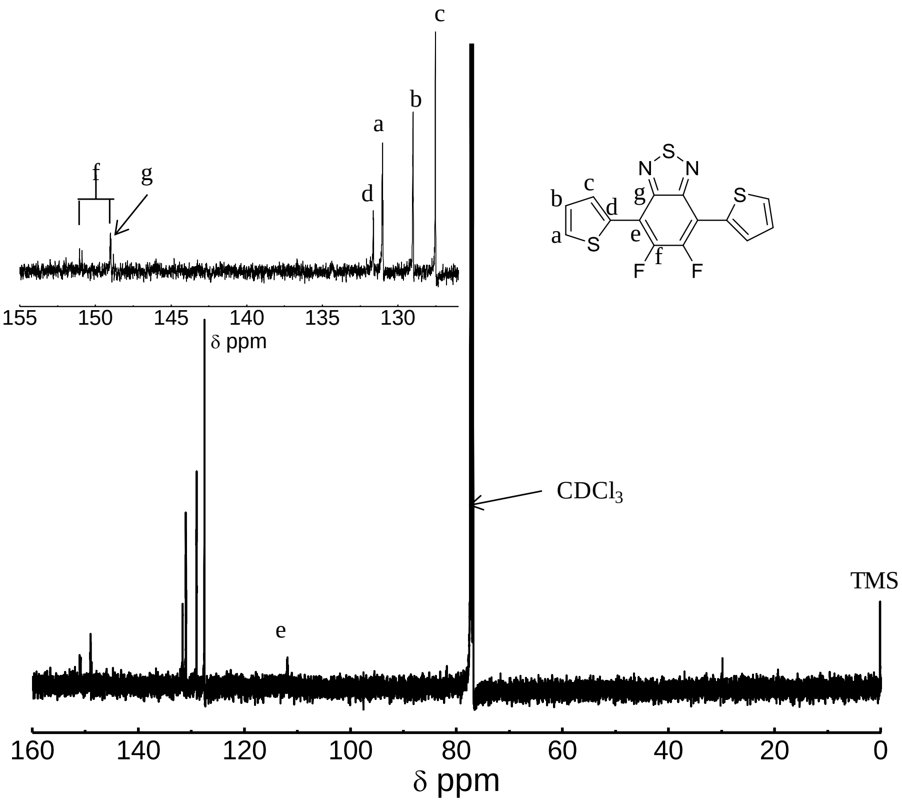


Fig. S 7^{13}C NMR spectrum of 5,6-difluoro-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (5)

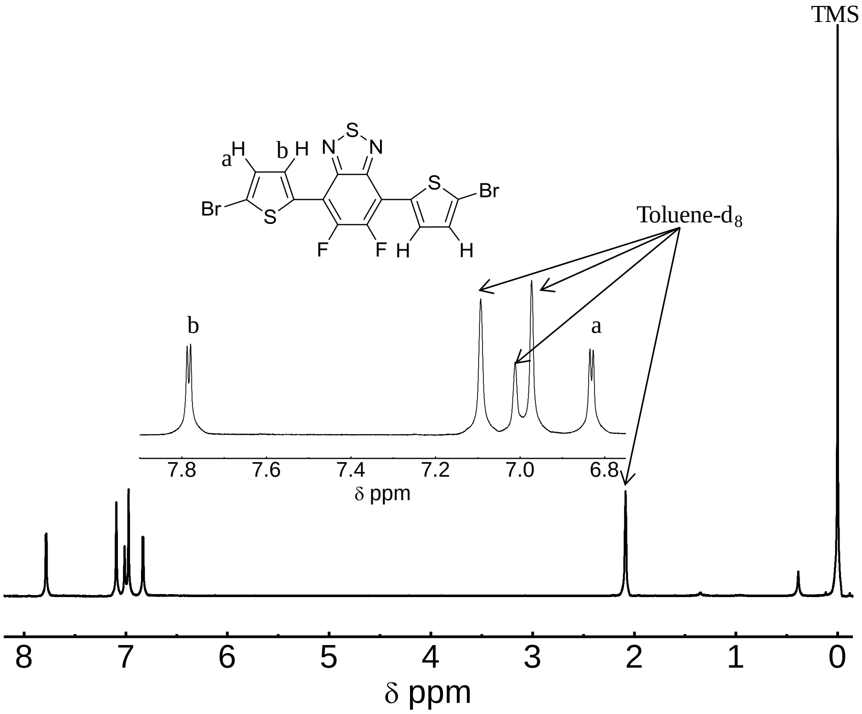


Fig. S 8 ^{1}H NMR spectrum of 4,7-bis(5-bromothiophen-2-yl)-5,6-difluorobenzo[*c*][1,2,5] thiadiazole at 90 °C in toluene-d_8 (6)

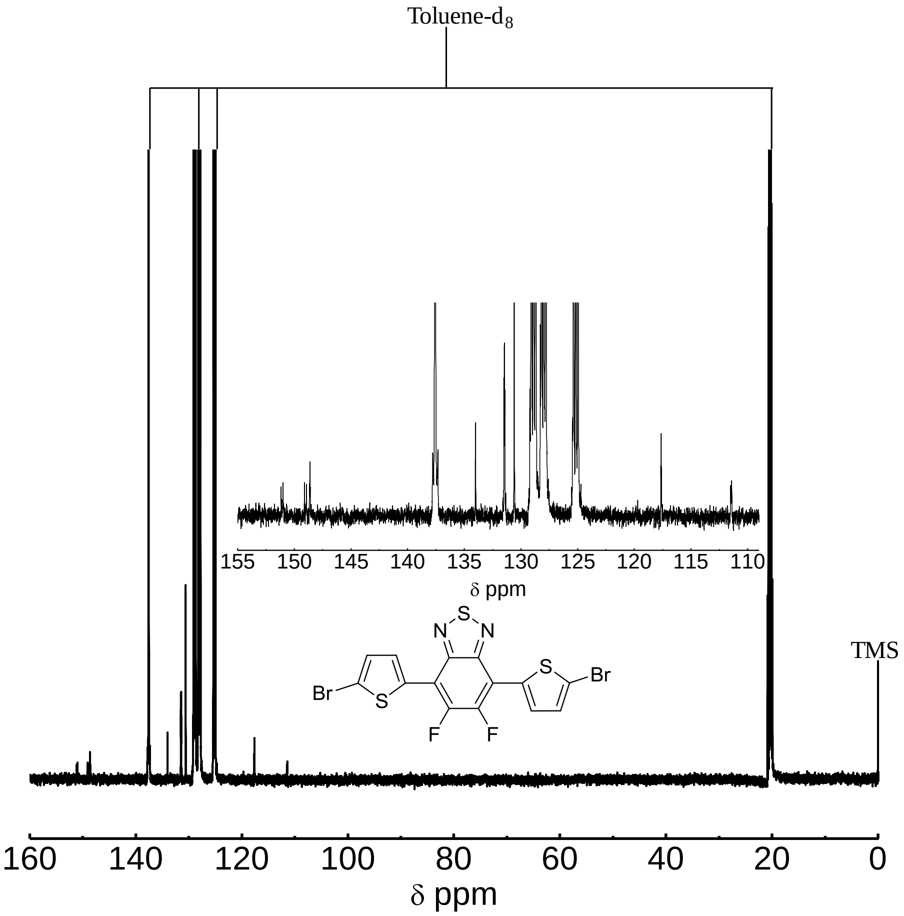


Fig. S 9 ^{13}C NMR spectrum of 4,7-bis(5-bromothiophen-2-yl)-5,6-difluorobenzo[*c*][1,2,5] thiadiazole at 90 °C in toluene-d_8 (6)

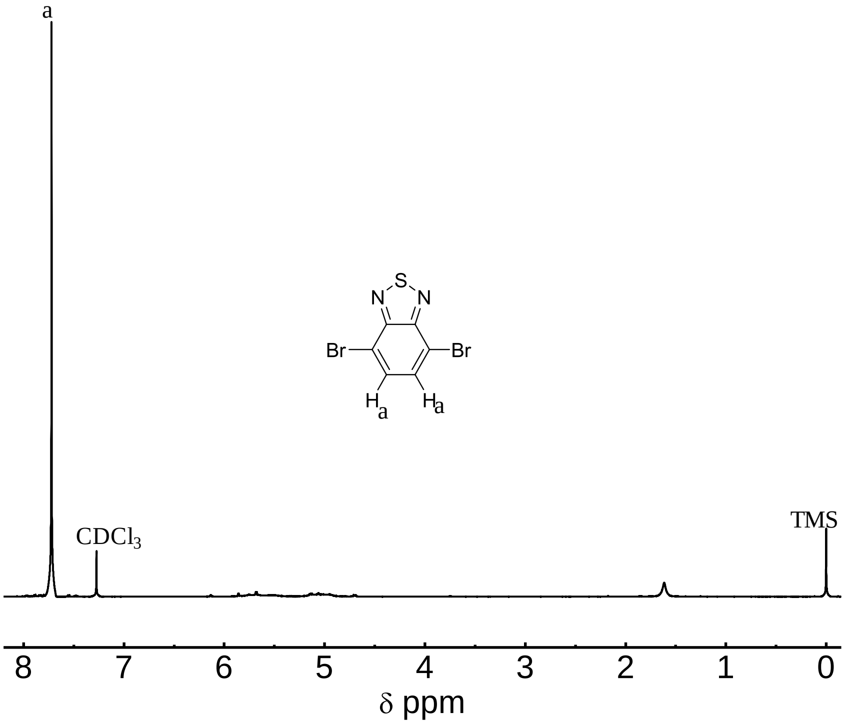


Fig. S 10 ^{1}H NMR spectrum of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (7)

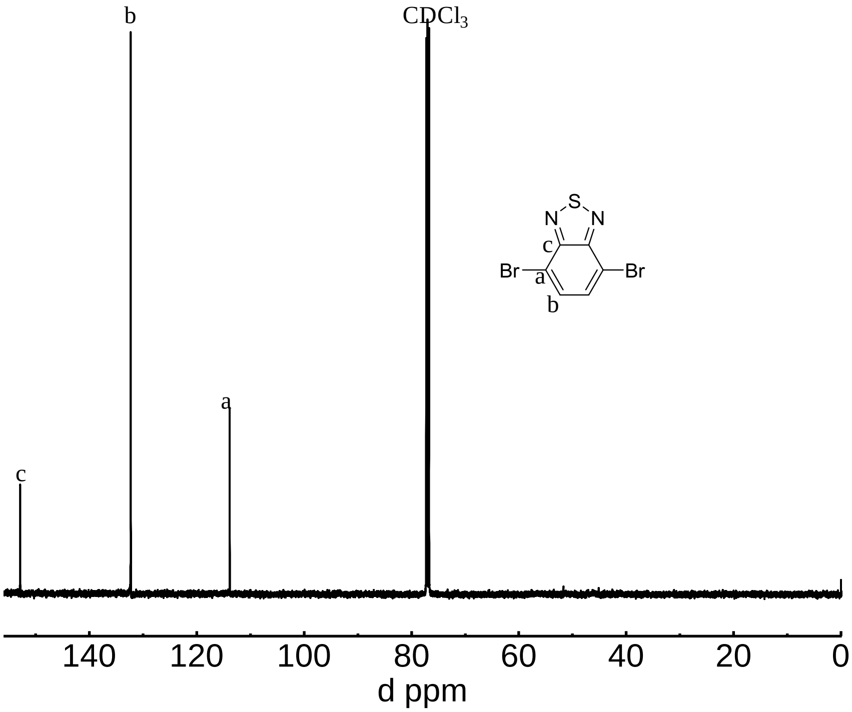


Fig. S 11 ^{13}C NMR spectrum of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (7)

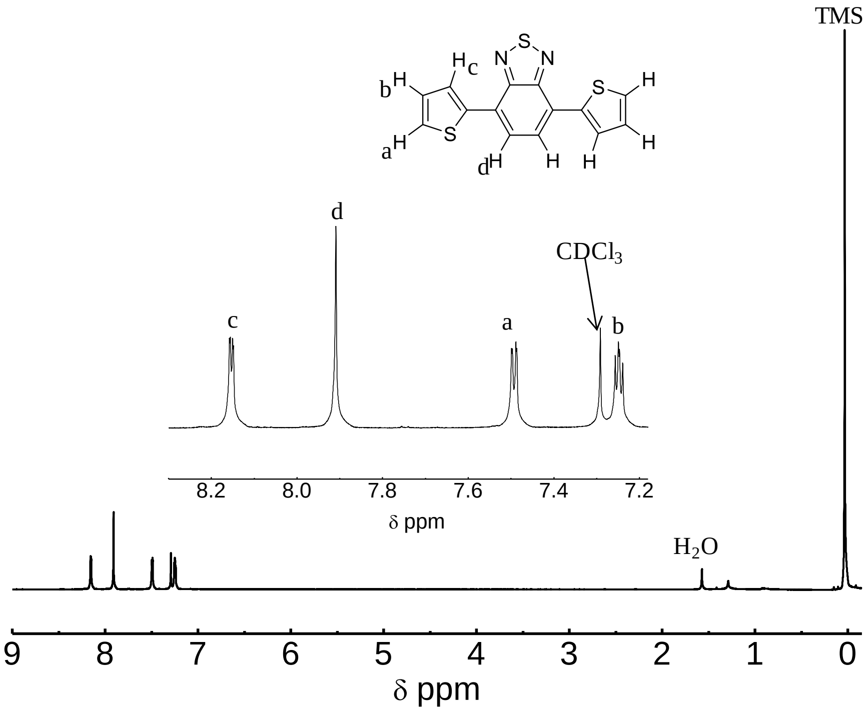


Fig. S 12 ^{1}H NMR spectrum of 4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (8)

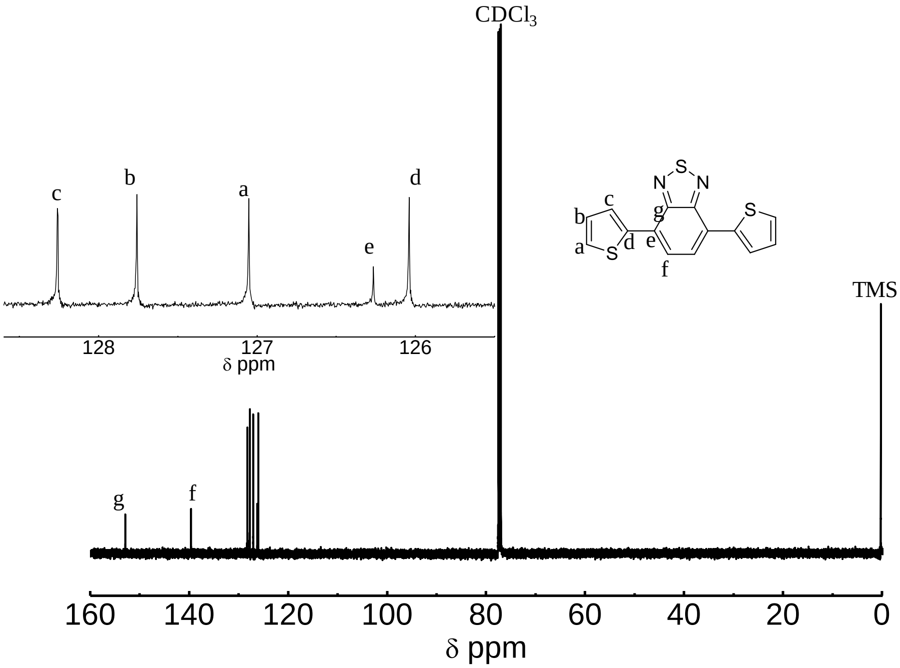


Fig. S 13 ^{13}C NMR spectrum of 4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (8)

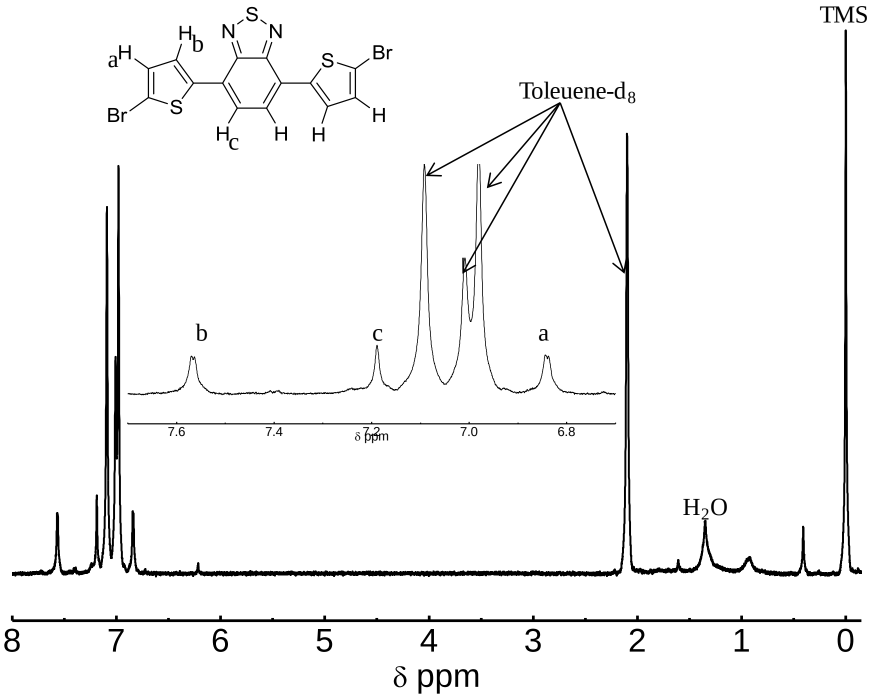


Fig. S 14 ^{1}H NMR spectrum of 4,7-bis(5-bromothiophen-2-yl)benzo[*c*][1,2,5]thiadiazole at 90 °C in toluene-d_8 (9**)**

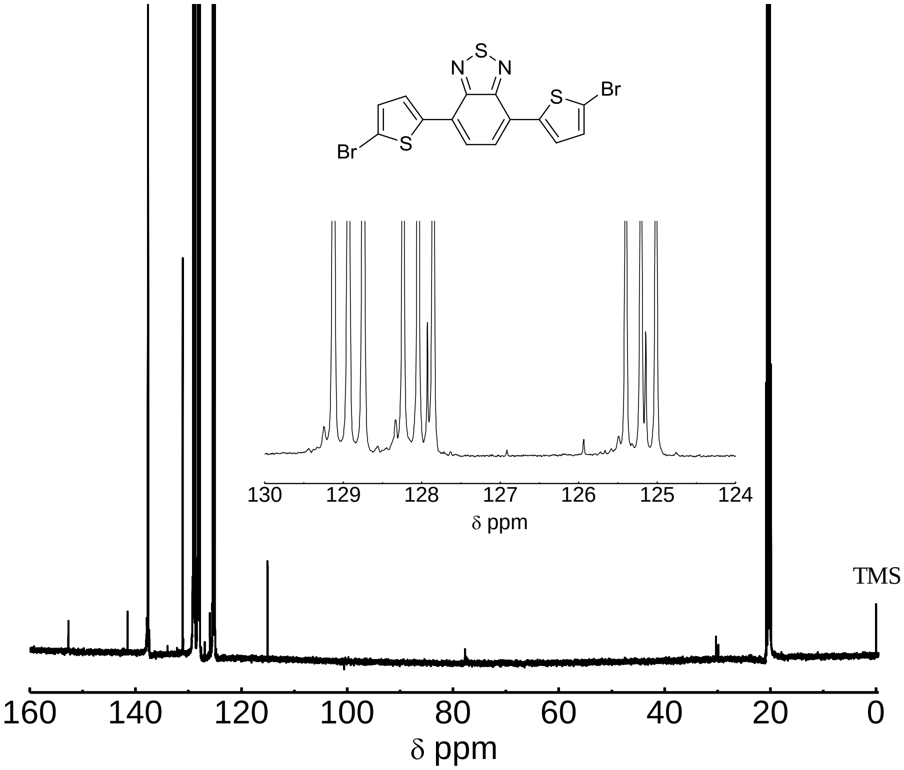


Fig. S 15 ^{13}C NMR spectrum of 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole at 90 °C in toluene-d_8 (9)

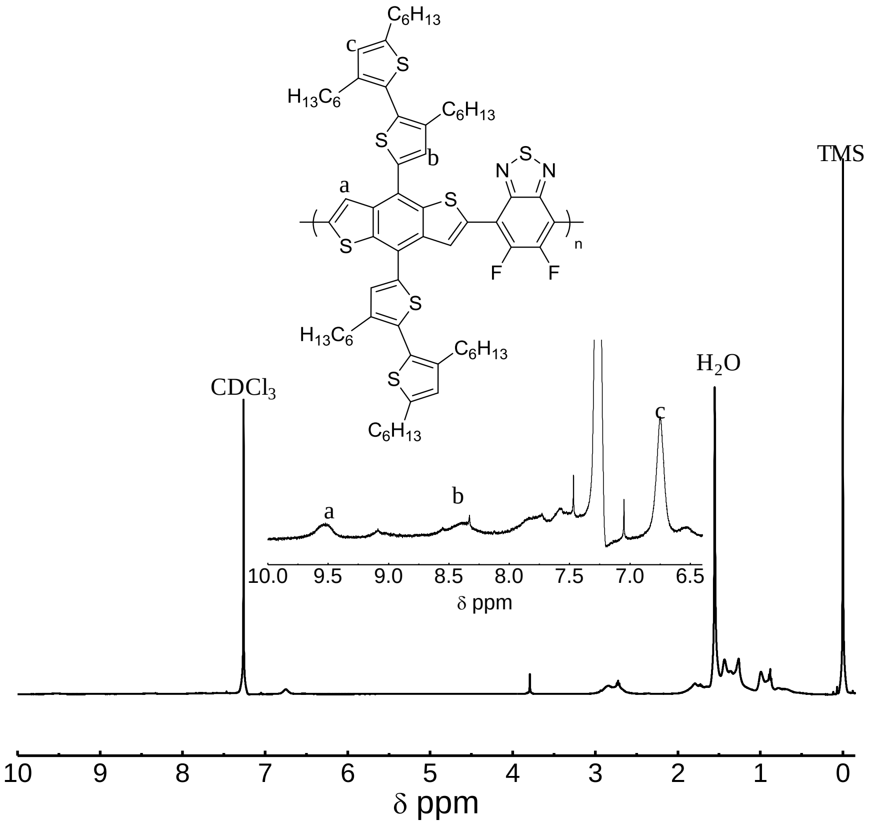


Fig. S 16 ^{1}H NMR spectrum of poly{4-(4,8-bis(3,3',5'-trihexyl-[2,2'-bithiophen]-5-yl)benzo[1,2-*b*:4,5-b']dithiophen-2-yl)-*alt*-5,6-difluorobenzo[*c*][1,2,5]thiadiazole} (**P1**)

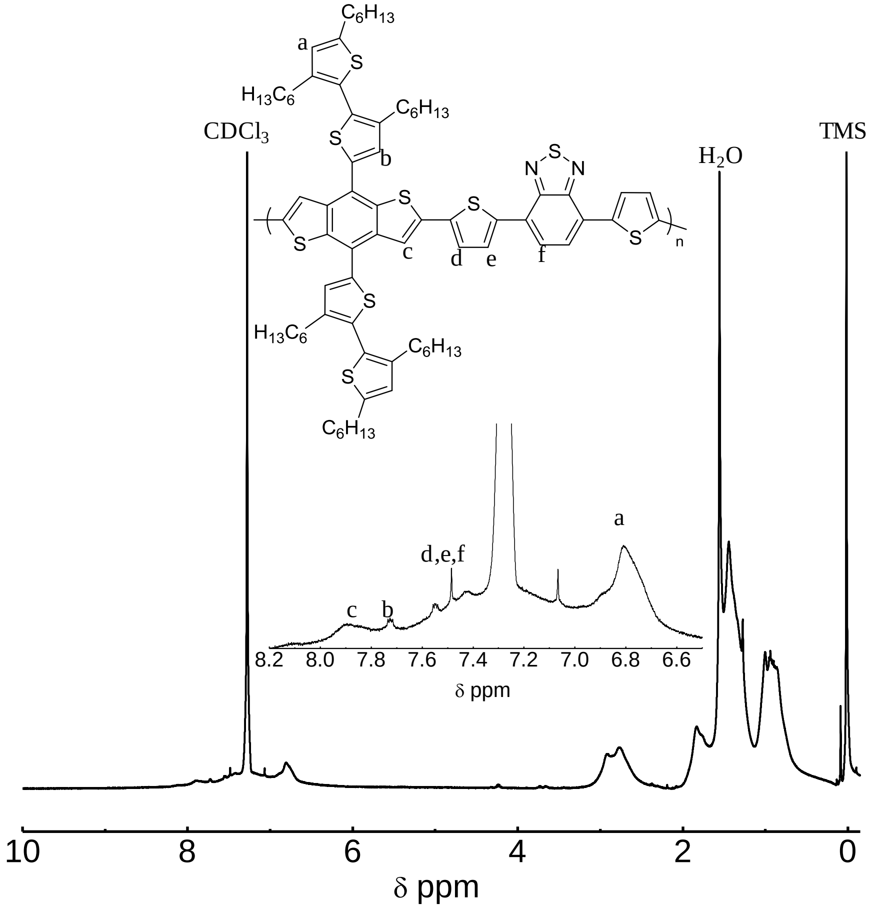


Fig. S 17 ^{1}H NMR spectrum of poly{4-(4,8-bis(3,3',5'-trihexyl-[2,2'-bithiophen]-5-yl) benzo[1,2-*b*:4,5-b']dithiophen-2-yl)-*alt*-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole} (**P2**)

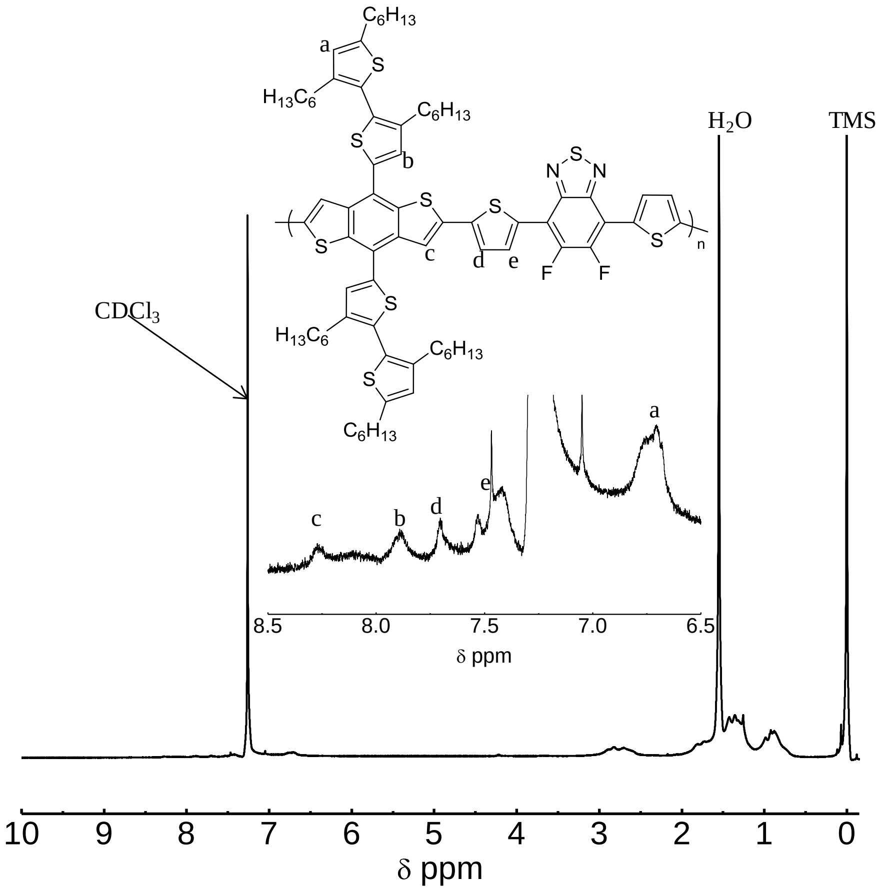
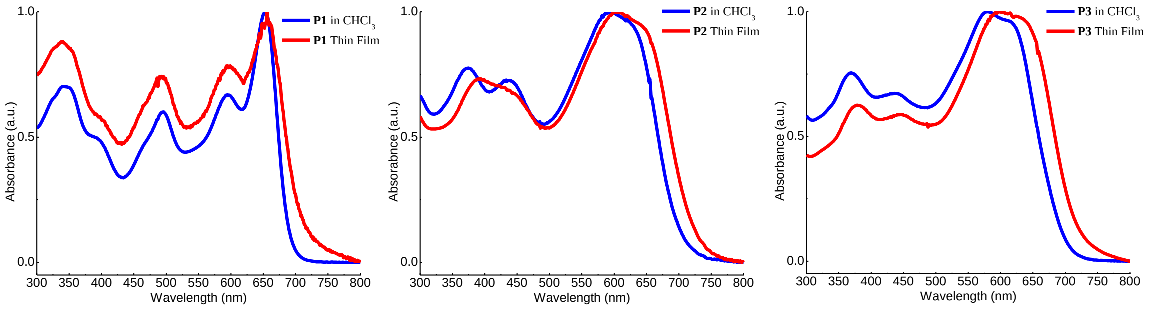


Fig. S 18 ^{1}H NMR spectrum of poly{4-(4,8-bis(3,3',5'-trihexyl-[2,2'-bithiophen]-5-yl)benzo[1,2-*b*:4,5-b']dithiophen-2-yl)-*alt*-4,7-di(thiophen-2-yl)-5,6-di(fluoro)benzo[*c*][1,2,5]thiadiazole} (**P3**)



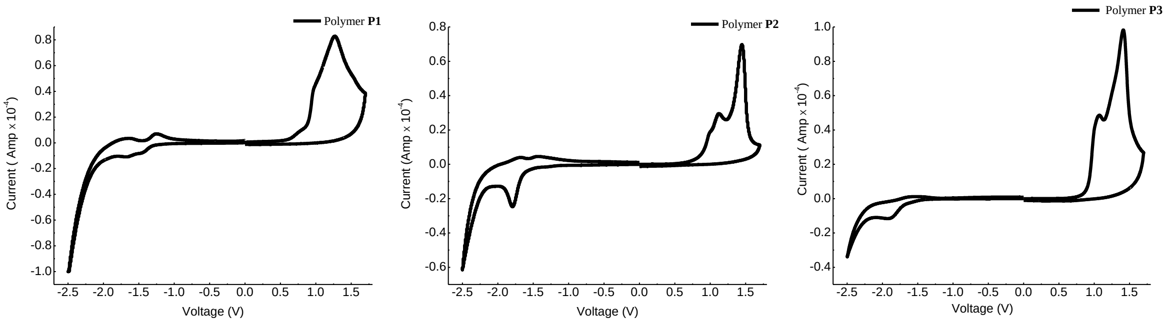
(a) (b) (c)

Fig. S 19 UV-Vis spectra of polymers **P1**, **P2**, and **P3**

Table S 1. Absorption coefficients of polymers **P1**, **P2**, and **P3**

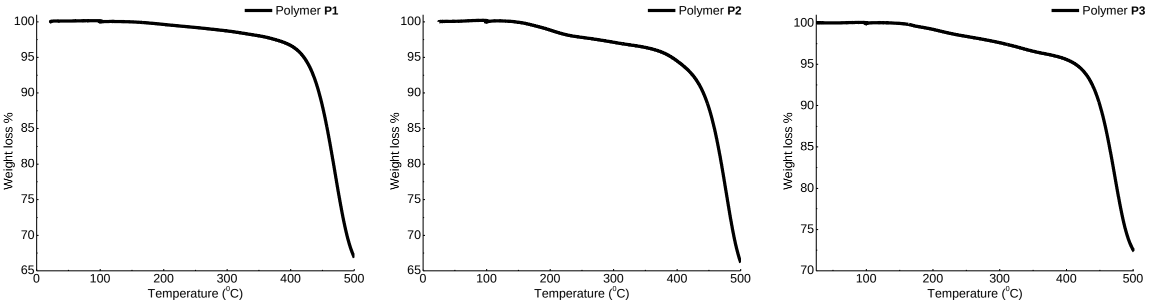
Polymer	Spin rate (rpm)	Average Absorbance[a]	Average Thickness of the Films[b] (× 10^{-7} cm)	ε (× 10^{4} cm)
P1	1000	0.1325	15.6	8.55
	800	0.1468	22.1	6.64
	600	0.1623	25.7	6.30
P2	1000	0.0822	8.58	9.59
	800	0.0840	11.7	7.20
	600	0.0938	12.5	7.53
P3	1000	0.1777	18.1	9.84
	800	0.1861	21.5	8.65
	600	0.2033	23.7	8.57

[a] average of three measurements, [b] average of ten measurements.



(a) (b) (c)

Fig. S 20 The cyclic voltammograms of polymers **P1**, **P2**, and **P3**



(a) (b) (c)

Fig. S 21 TGA thermograms for polymers **P1**, **P2**, and **P3**

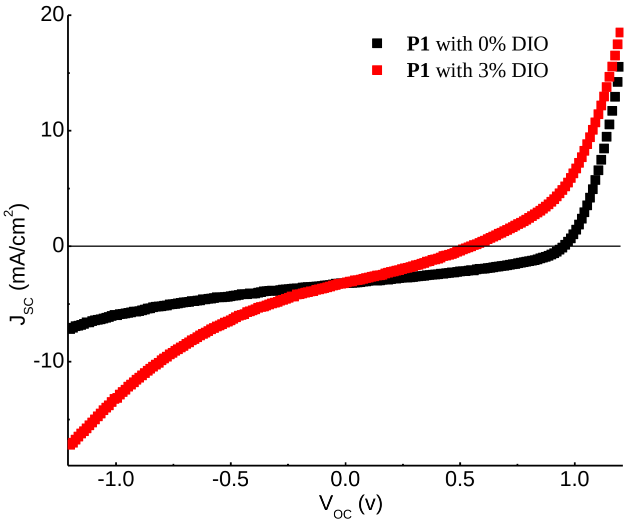


Fig. S 22 J-V curve for polymer **P1**

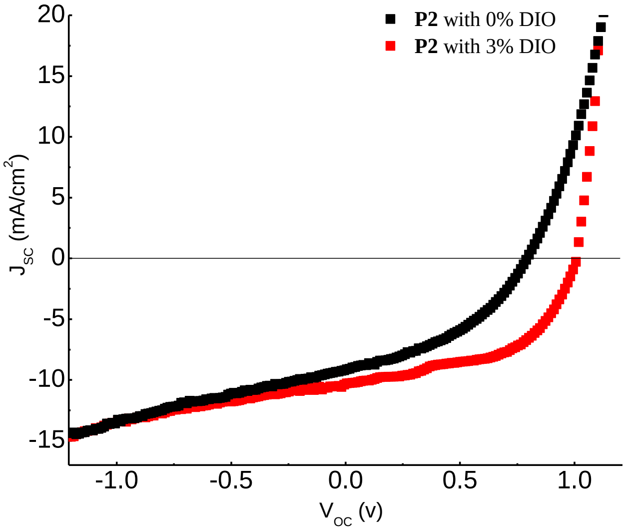


Fig. S 23 J-V curve for polymer **P2**

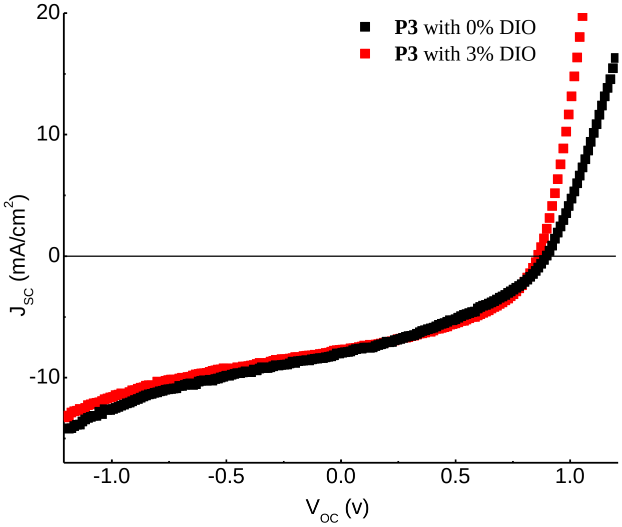


Fig. S 24 J-V curve for polymer **P3**

Table S 2 Photovoltaic properties of **P1** with DIO as an additive in solar cell devices (the values in brackets represent average values)

DIO	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)	Thickness (nm)
0	0.96 (0.92)	3.20 (3.14)	0.39 (0.36)	1.19 (1.06)	81.44
1	0.85 (0.78)	3.03 (3.13)	0.30 (0.29)	0.78 (0.73)	76.23
2	0.59 (0.45)	3.01 (2.95)	0.32 (0.28)	0.57 (0.39)	79.05
3	0.55 (0.44)	3.19 (3.22)	0.29 (0.29)	0.51 (0.41)	79.97
4	0.42 (0.33)	2.91 (2.90)	0.31 (0.28)	0.38 (0.29)	69.15
5	0.28 (0.30)	3.22 (0.30)	0.27 (0.25)	0.25 (0.23)	75.50

Table S 3 Photovoltaic properties of **P2** with DIO as an additive in solar cell devices (the values in brackets represent average values)

DIO	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)	Thickness (nm)
0	0.91 (0.85)	7.90 (8.33)	0.42 (0.40)	2.96 (2.84)	87.89
1	0.79 (0.81)	9.07 (8.70)	0.40 (0.40)	2.85 (2.79)	79.77
2	0.92 (0.82)	7.42 (8.02)	0.51 (0.47)	3.45 (3.13)	79.65
3	1.03 (0.85)	7.05 (8.22)	0.48 (0.49)	3.52 (3.43)	78.37
4	0.88 (0.83)	7.29 (7.85)	0.54 (0.51)	3.46 (3.36)	78.23
5	0.76 (0.75)	7.99 (7.94)	0.54 (0.54)	3.29 (3.23)	75.77

Table S 4 Photovoltaic properties of **P3** with DIO as an additive in solar cell devices (the values in brackets represent average values)

DIO	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)	Thickness (nm)
0	0.90 (0.91)	8.03 (7.81)	0.36 (0.37)	2.67 (2.61)	79.11
1	0.86 (0.89)	6.92 (7.18)	0.45 (0.39)	2.69 (2.50)	79.57
2	0.86 (0.88)	7.42 (7.25)	0.42 (0.40)	2.71 (2.55)	78.47
3	0.86 (0.86)	7.72 (7.57)	0.43 (0.43)	2.93 (2.82)	85.05
4	0.88 (0.84)	7.25 (7.24)	0.40 (0.40)	2.56 (2.47)	83.71
5	0.85 (0.82)	6.35 (6.10)	0.46 (0.46)	2.50 (2.33)	79.06

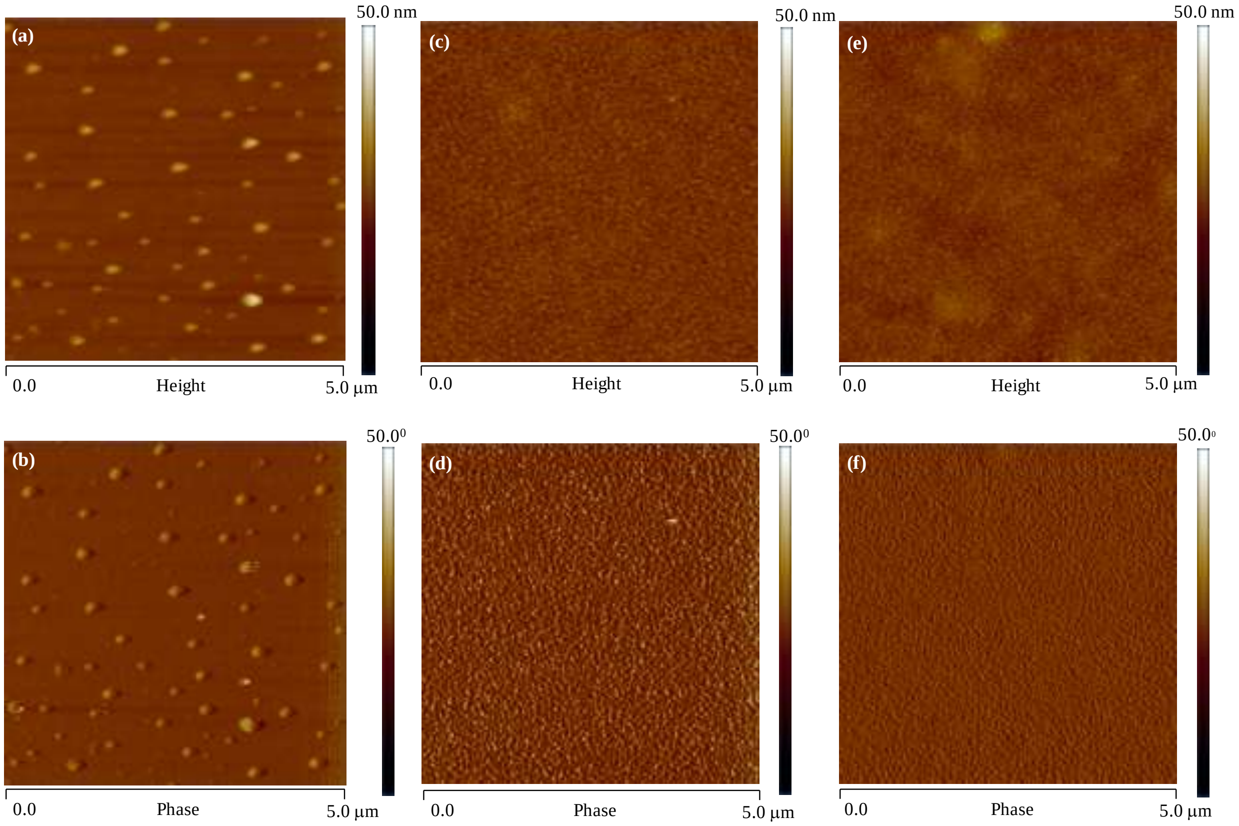


Fig. S 25 TMAFM images of the solar cell devices without DIO: (a) height,(b) phase polymer **P1**:PC$_{71}$BM = 1:1 blend, (c) height, (d) phase of polymer **P2**:PC$_{71}$BM =1:1 blend and (e) height , (f) phase of polymer **P3**:PC$_{71}$BM 1:1 blend; scan size (5 μm × 5 μm).

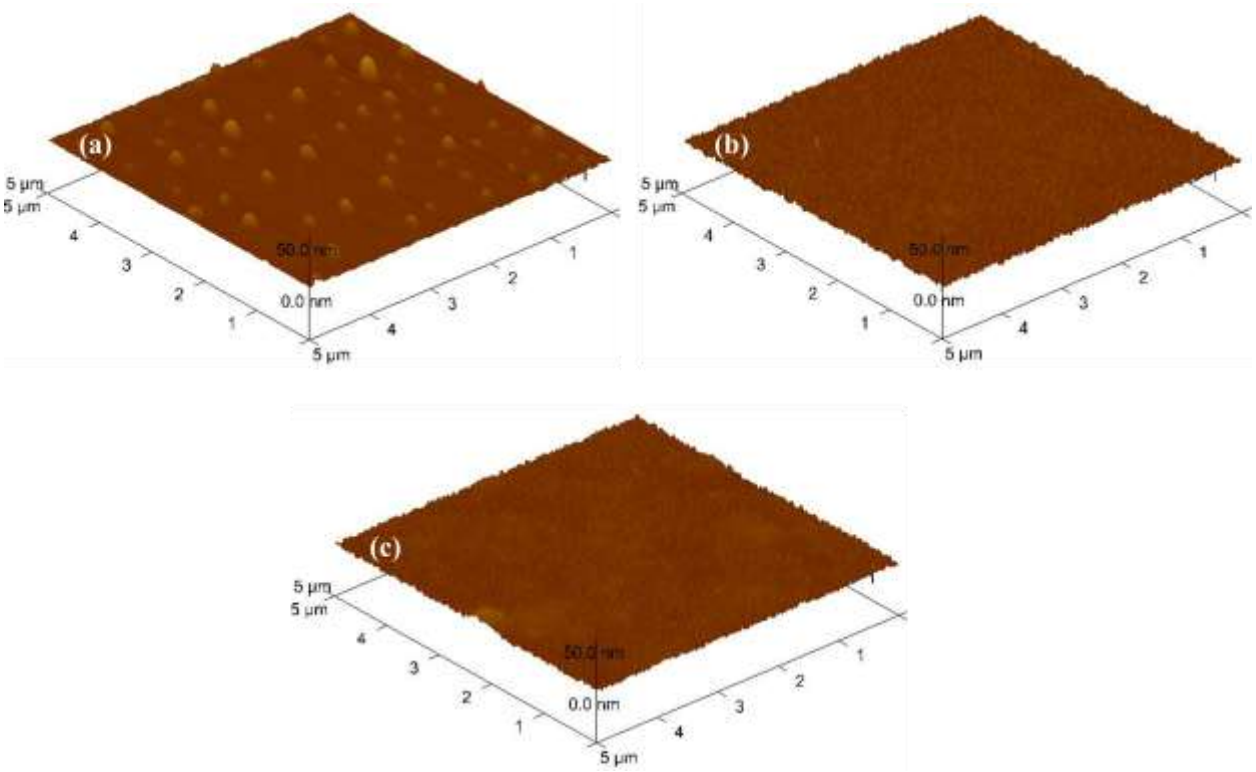


Fig. S 26 3D TMAFM phase images of the solar cell devices without DIO: (a) polymer **P1**:PC$_{71}$BM = 1:1blend (rms=1.46 nm); (b) polymer **P2**:PC$_{71}$BM =1:1 blend (rms=1.15 nm); and (c) polymer **P3**:PC$_{71}$BM 1:1 blend (rms=1.22 nm); scan size (5 µm × 5 µm)

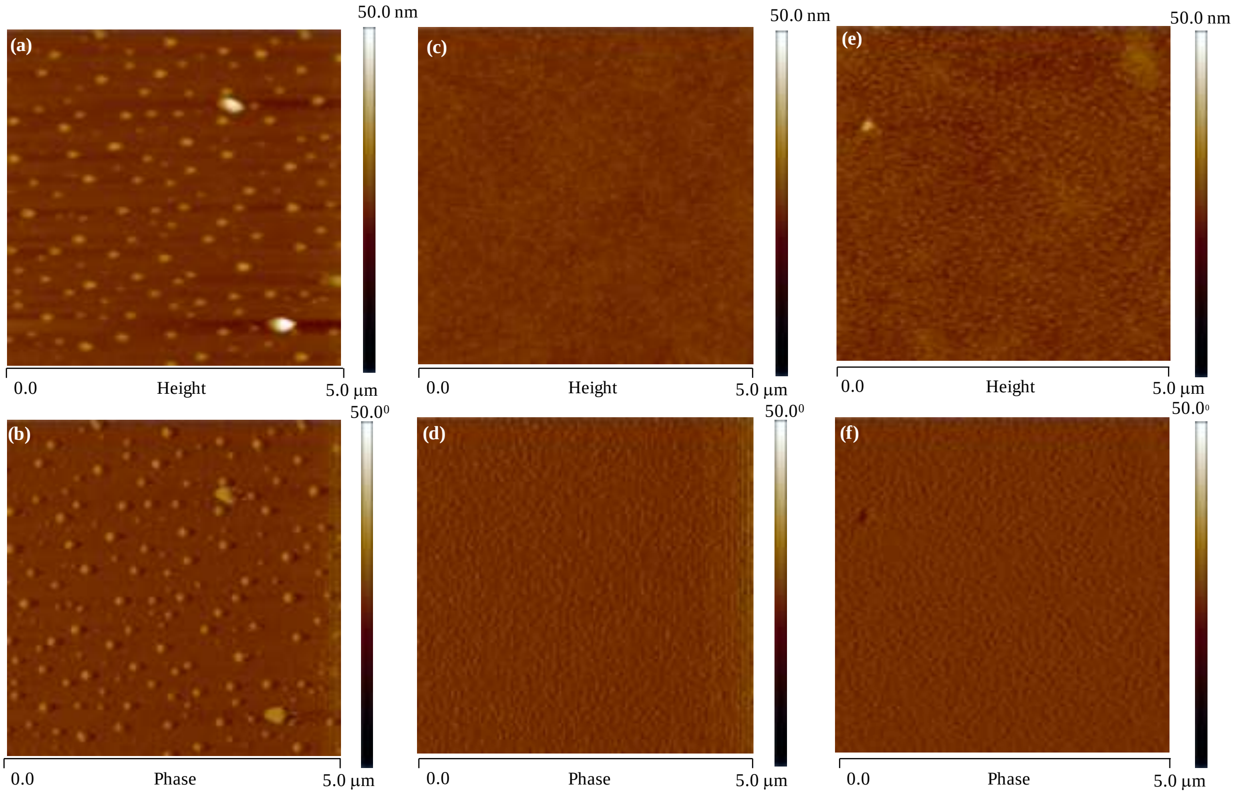


Fig. S 27 TMAFM images of the solar cell devices with 3% v/v DIO: (a) height,(b) phase polymer **P1:**$PC_{71}BM$ = 1:1 blend, (c) height, (d) phase of polymer **P2**:$PC_{71}BM$ =1:1 blend and (e) height , (f) phase of polymer **P3**:$PC_{71}BM$ 1:1 blend; scan size (5 µm × 5 µm).

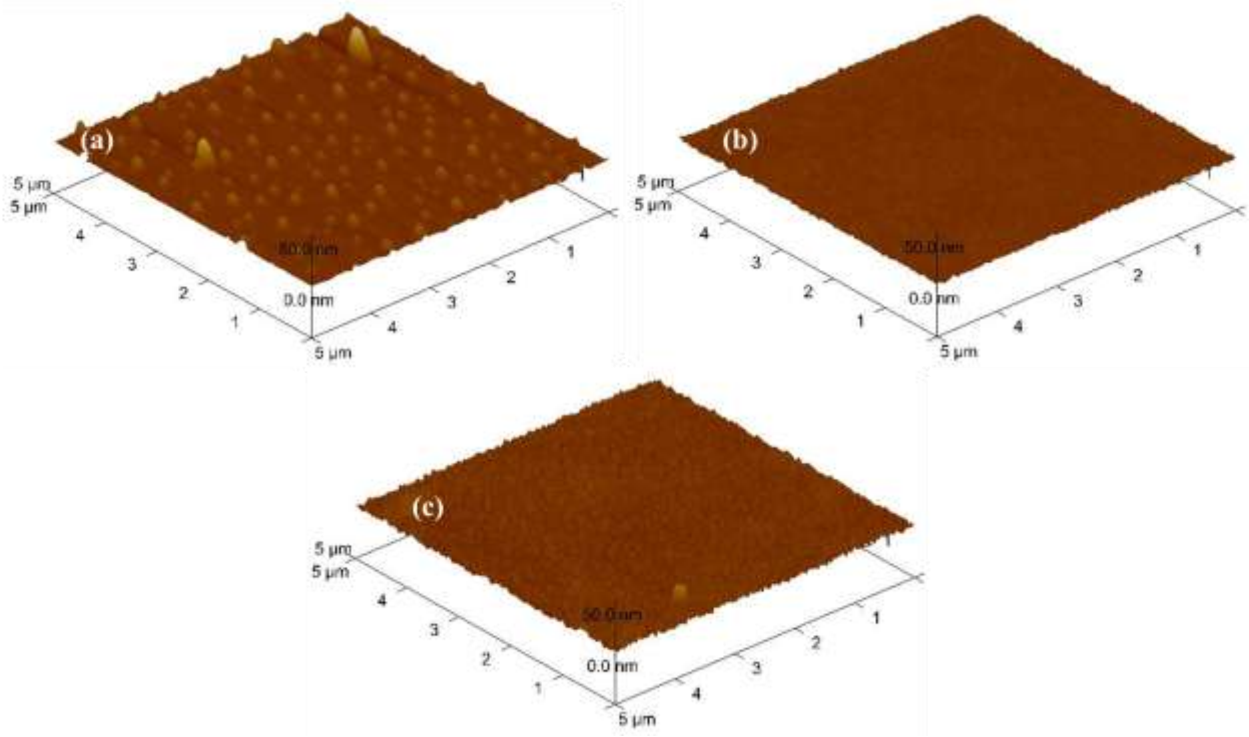
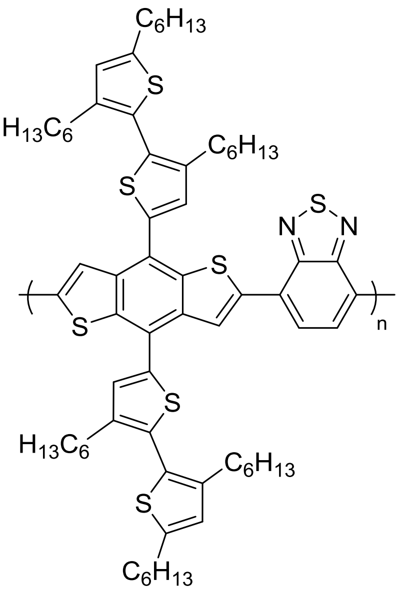


Fig. S 28 3D TMAFM phase images of the solar cell devices with 3% DIO: (a) polymer **P1**:$PC_{71}BM$ = 1:1blend (rms-2.08); (b) polymer **P2**:$PC_{71}BM$ =1:1 blend (rms=0.88);and (c) polymer **P3**:$PC_{71}BM$=1:1 blend (rms=1.24 nm); scan size (5 µm × 5 µm)

Table S 5 Optoelectronic properties and photovoltaic properties of polymer **P1'**[3]

Polymer	M_n^a(PDI) (g/mol)	HOMO[b] (eV)	LUMO[c] (eV)	E_g (eV)	P:PCBM	V_{oc}(V)	J_{sc} (mA/cm2)	FF	PCE (%)
P1'	40800 (4.4)	-5.53	-3.57	1.97	1:3	0.99	5.36	0.47	2.54



P1'

Fig. S 29 Chemical Structure of poly{4-(4,8-bis(3,3',5'-trihexyl-[2,2'-bithiophen]-5-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)-alt-benzo[c][1,2,5]thiadiazole} **P1'**[3]

Table S 6 Photovoltaic properties of **P3** with DIO as an additive in solar cell devices[3]

Polymer	**DIO (%)**	**V_{OC} (V)**	**J_{SC} (mA/cm^2)**	**FF**	**PCE (%)**
P1'[a]	0	1.00	5.36	0.47	2.54
	1	0.98	5.32	0.41	2.17
	3	0.78	4.88	0.31	1.21
	5	0.79	4.78	0.34	1.28

[a] **P1'**:$PC_{61}BM$=1:3

1. H. Zhou, L. Yang, A. C. Stuart, S. C. Price, S. Liu and W. You, *Angew. Chem., Int. Ed.*, 2011, **50**, 2995-2998, S2995/2991-S2995/2916.
2. F. Wu, D. Zha, L. Chen and Y. Chen, *J.Polym. Sci. Part A: Polym. Chem.*, 2013, **51**, 1506-1511.
3. R. S. Kularatne, P. Sista, H. Q. Nguyen, M. P. Bhatt, M. C. Biewer and M. C. Stefan, *Macromolecules*, 2012, **45**, 7855-7862.