Supporting Information

for

Direct arylation polycondensation for synthesis of bithiophene-based alternating copolymers

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Table 1. Optimization for the synthesis of **Polymer 7**[a]

Entry	Concentration of monomers	Reaction time(h)	M_n[b]	M_w/M_n[b]	Yield (%)[c]
1	0.30 M	1 h	12 900	1.91	81
2	0.15 M	0.5 h	15 200	2.10	85
3	0.075 M	1 h	11 700	2.07	83
4	0.15 M	6 h	18 100	2.35	96[d]

[a] Reactions were carried out at 100 °C using $Pd(OAc)_2$ (2 mol%), PivOH (30 mol%) and K_2CO_3 (2.5 equiv.) in DMAc. [b] Estimated by GPC calibrated on polystyrene standards. [c] The products were obtained by reprecipitation from $CHCl_3$/MeOH and washing with hexane. [d] Yield after Soxhlet extraction with hexane and acetone.

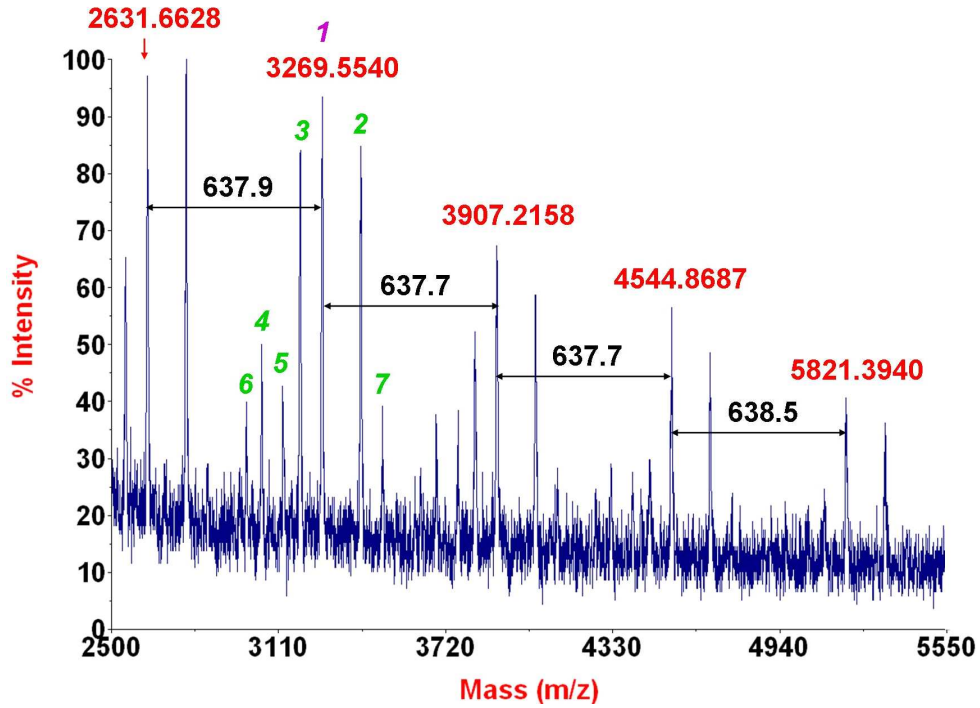
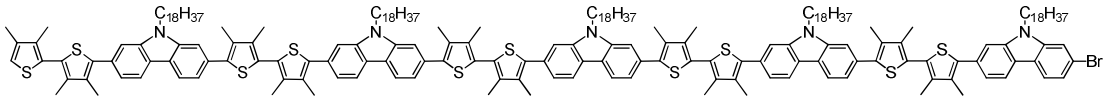


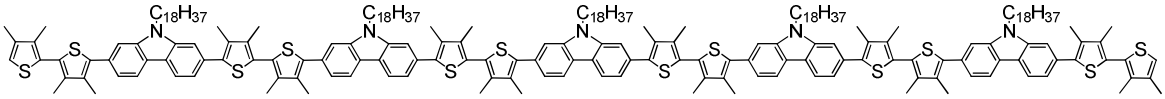
Figure S-1. MALDI-TOF-MASS spectrum of **Polymer 2** (Table 1, Entry 4) using dithranol as a matrix and des-Arg[1]-Bradykinin, Anglotensin I and Glu[1]-Flibrinopeptide B as external standards. The calculated mass for the repeating unit is 637.4. The m/z values for peaks 1-7 and their proposed assignment are shown as follows.

Peak 1, Found m/z: **3269.5540**



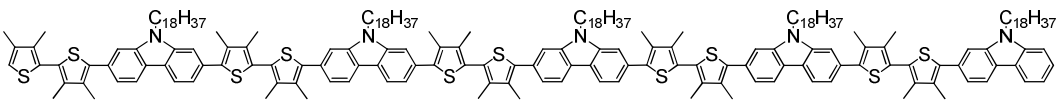
Calculated mass: **3268.82082**

Peak 2, Found m/z: **3410.2415**



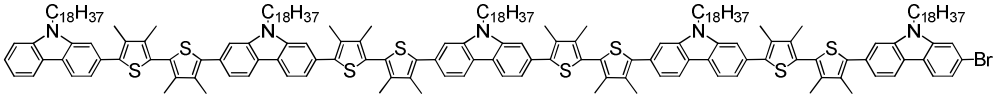
Calculated mass: **3410.94835**

Peak 3, Found m/z: **3189.0254**



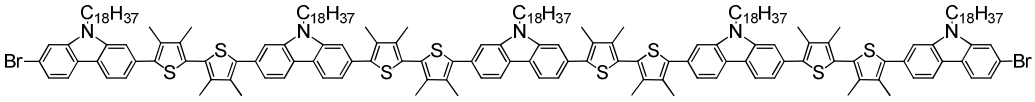
Calculated mass: **3190.91031**

Peak 4, Found m/z: **3048.4768**



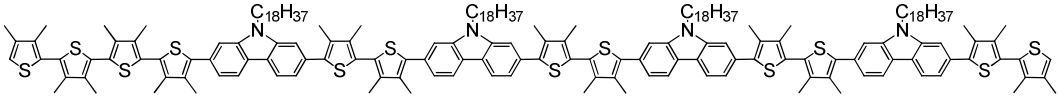
Calculated mass: **3048.78278**

Peak 5, Found m/z: **3126.5745**

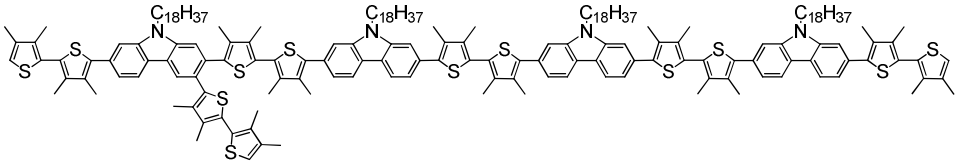


Calculated mass: **3128.69124**

Peak 6, Found m/z: **2992.4038**

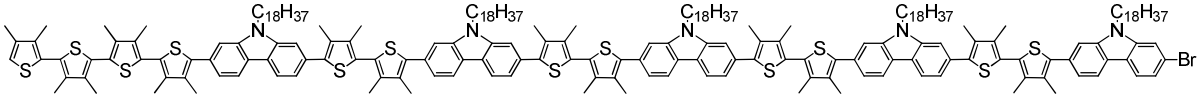


Or

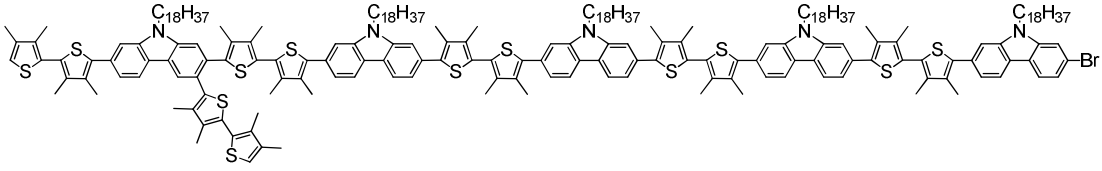


Calculated mass: **2993.60880**

Peak 7, Found m/z: **3489.0618**



Or



Calculated mass: **3488.85886**

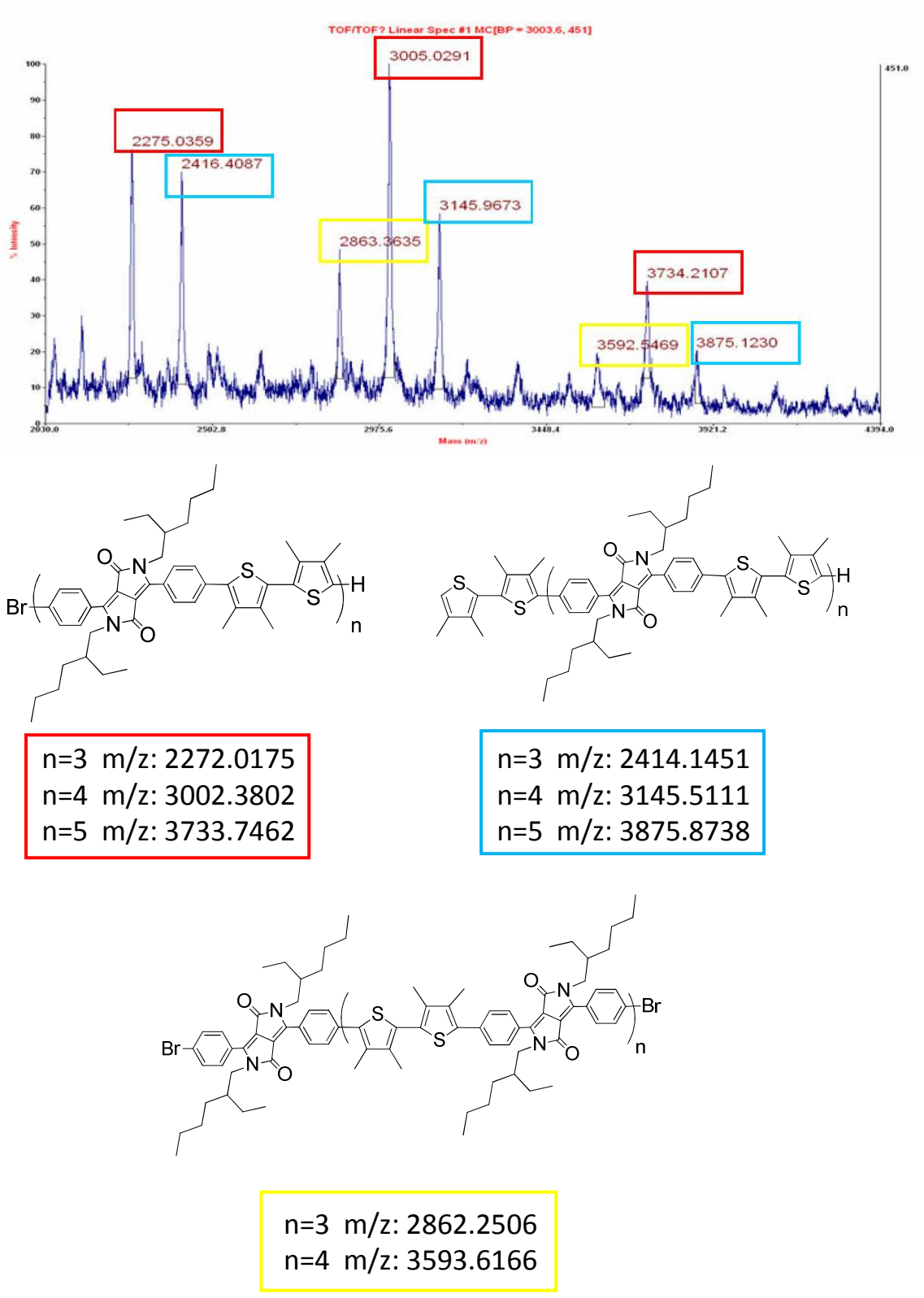
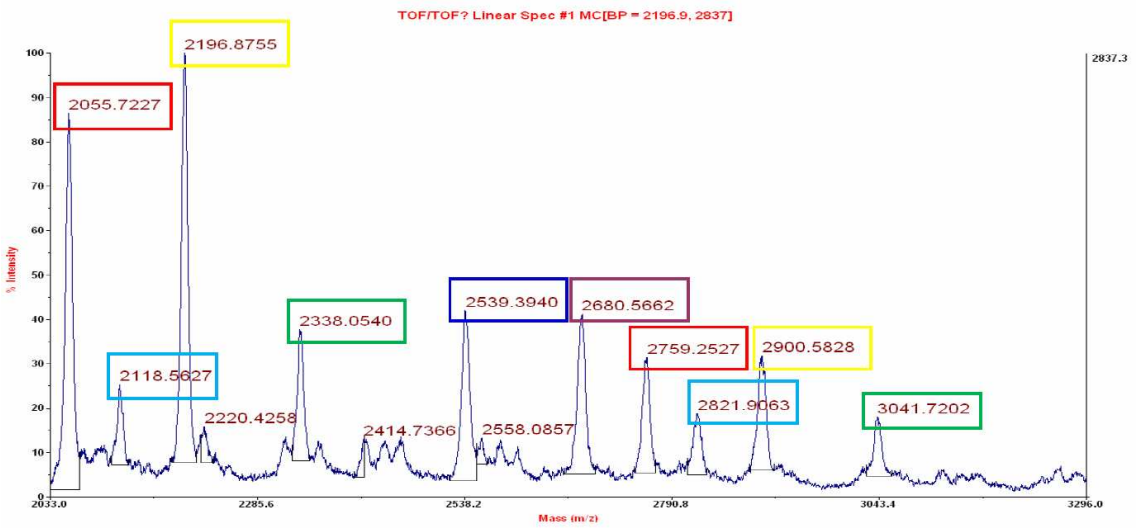
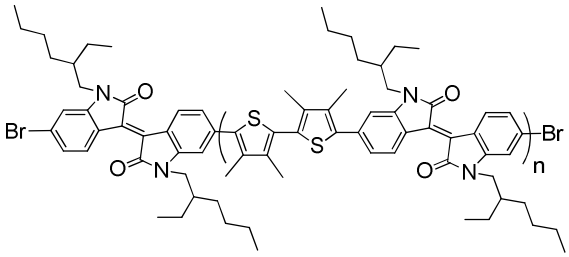
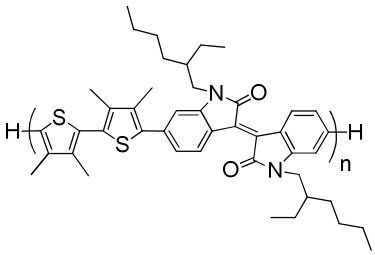


Figure S-2. MALDI-TOF-MASS spectrum of **Polymer 7** and proposed structures corresponding to the peaks.

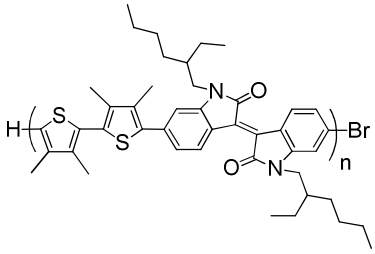




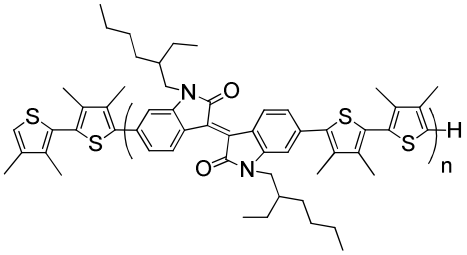
n=2 m/z: 2053.8410
n=3 m/z: 2758.1880



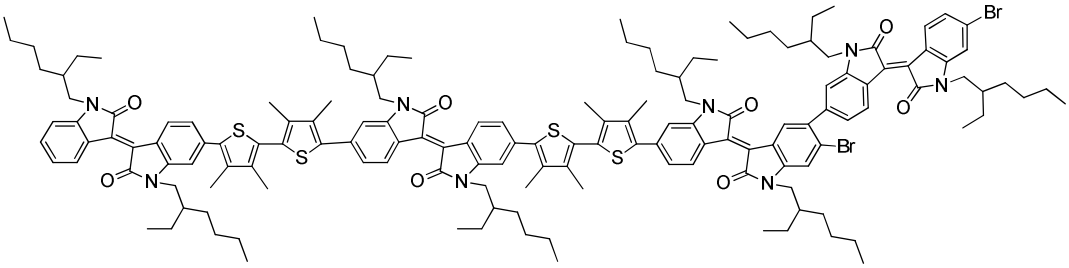
n=3 m/z: 2116.0601
n=4 m/z: 2820.4071



n=3 m/z: 2193.9706
n=4 m/z: 2898.3176



n=3 m/z: 2336.0981
n=4 m/z: 3041.4485



m/z: 2538.1500

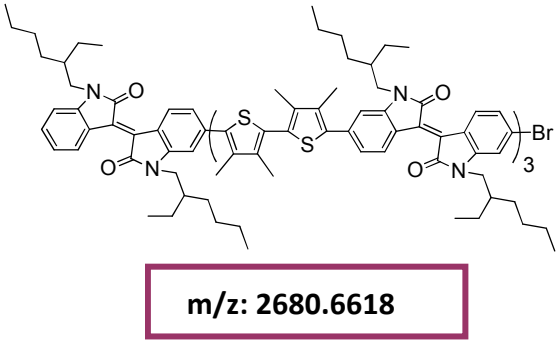


Figure S-3. MALDI-TOF-MASS spectrum of **Polymer 8** and proposed structures corresponding to the peaks.

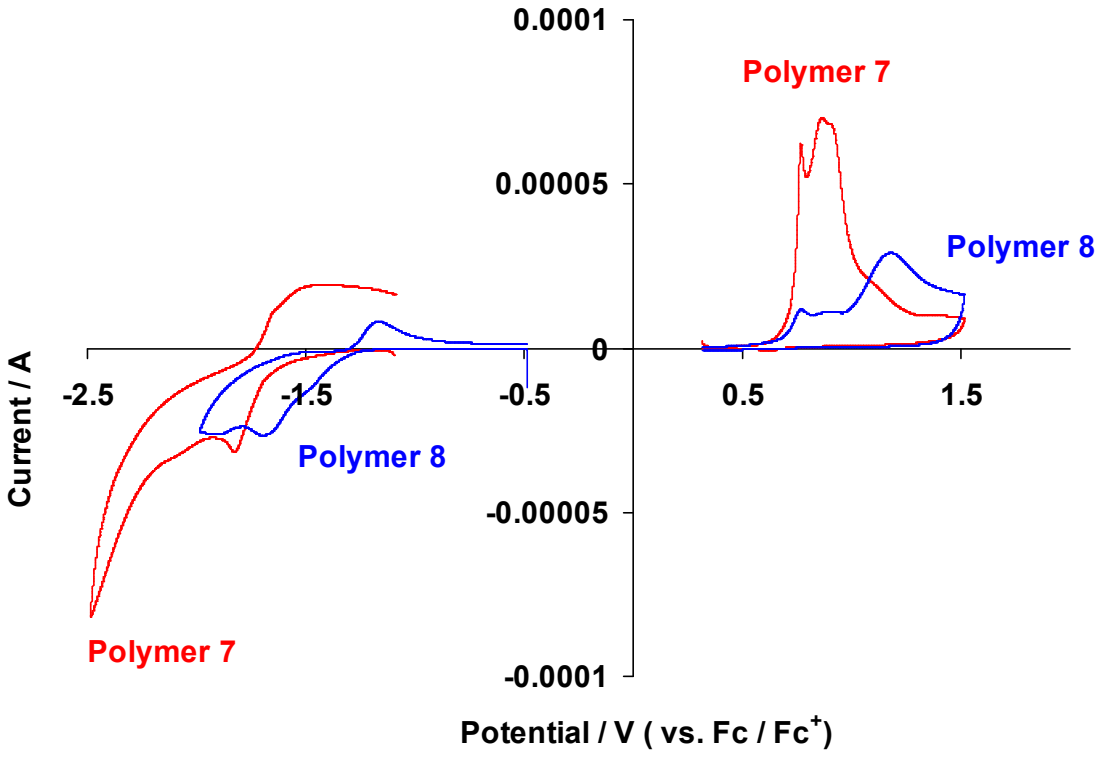


Figure S-4. Cyclic voltammograms of **Polymer 7** and **8** in CH_3CN containing Bu_4NPF_6 (0.1 M). Sweep rate = 10 mVs^{-1}.

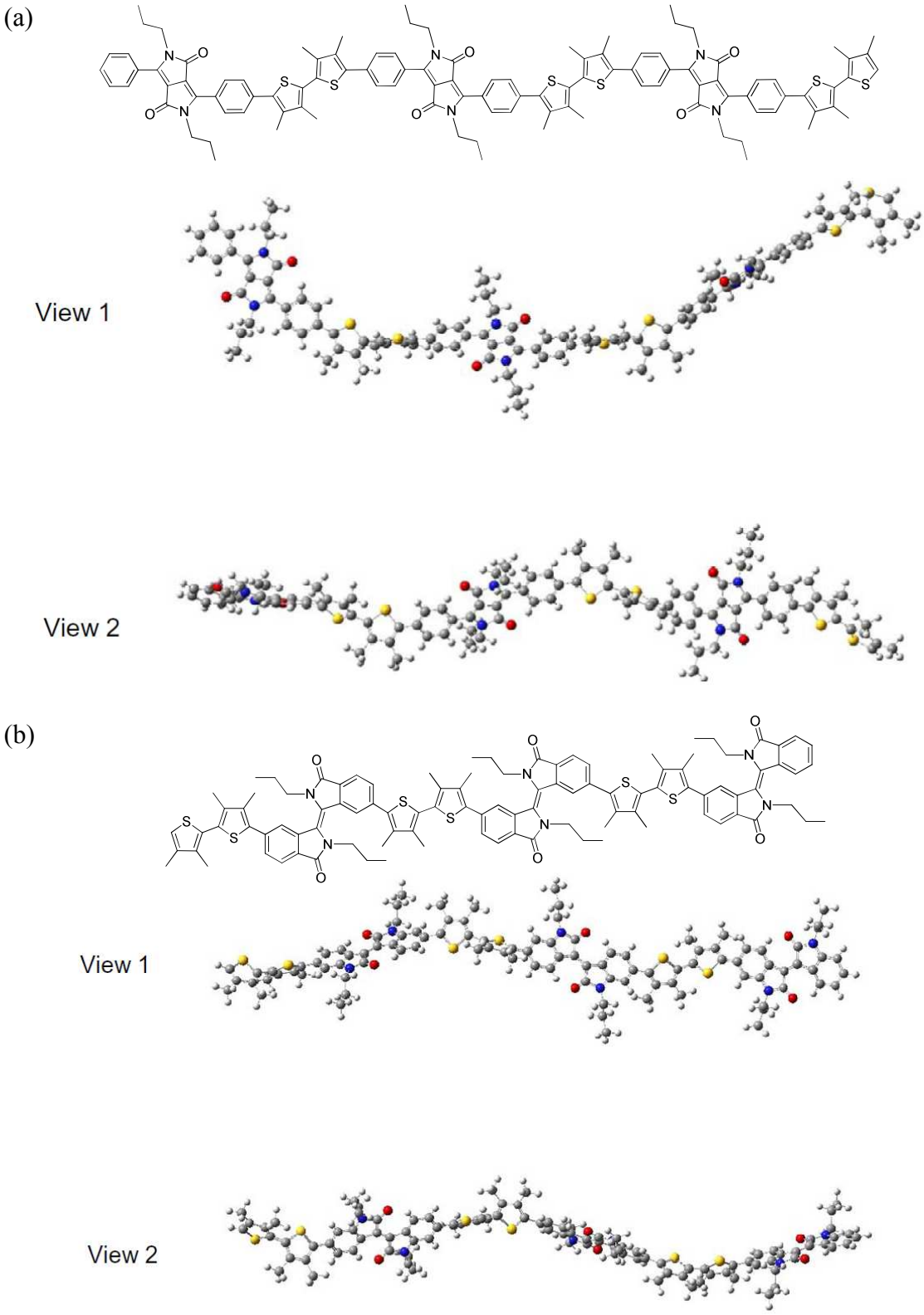


Figure S-5. Optimized structure of the models for (a) **Polymer 7** and (b) **Polymer 8** on the basis of the DFT calculation.

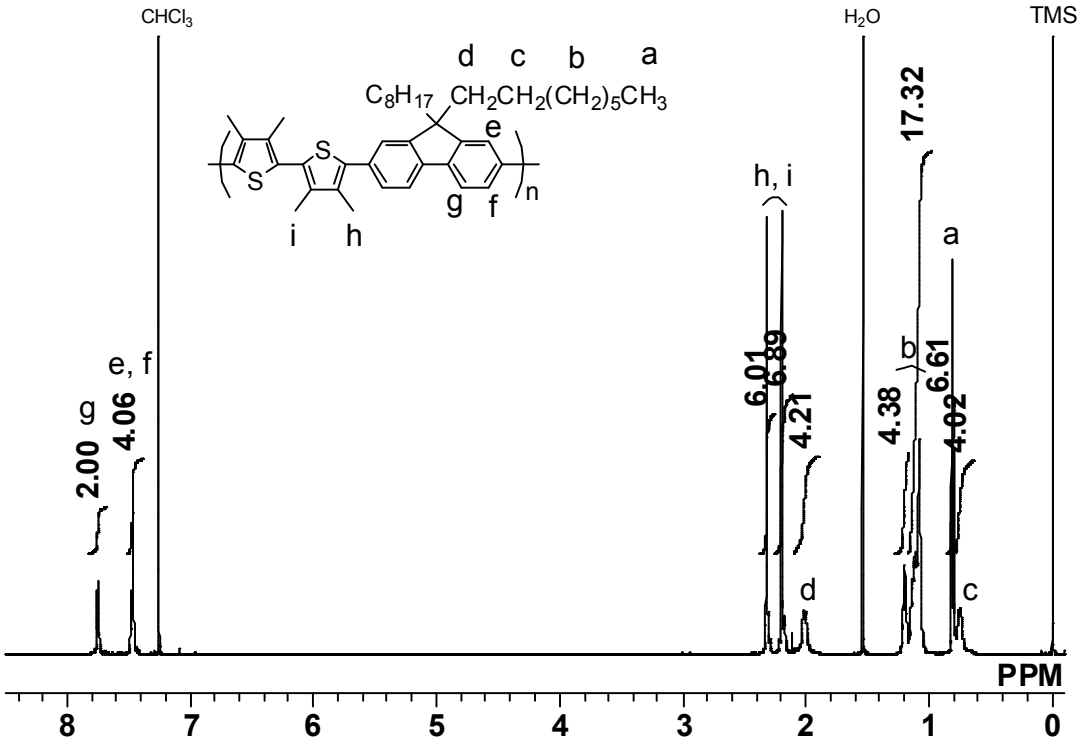


Figure S-6. ^{1}H NMR spectrum of **Polymer 1** (Table 1, Entry 2) (400 MHz, $CDCl_3$).

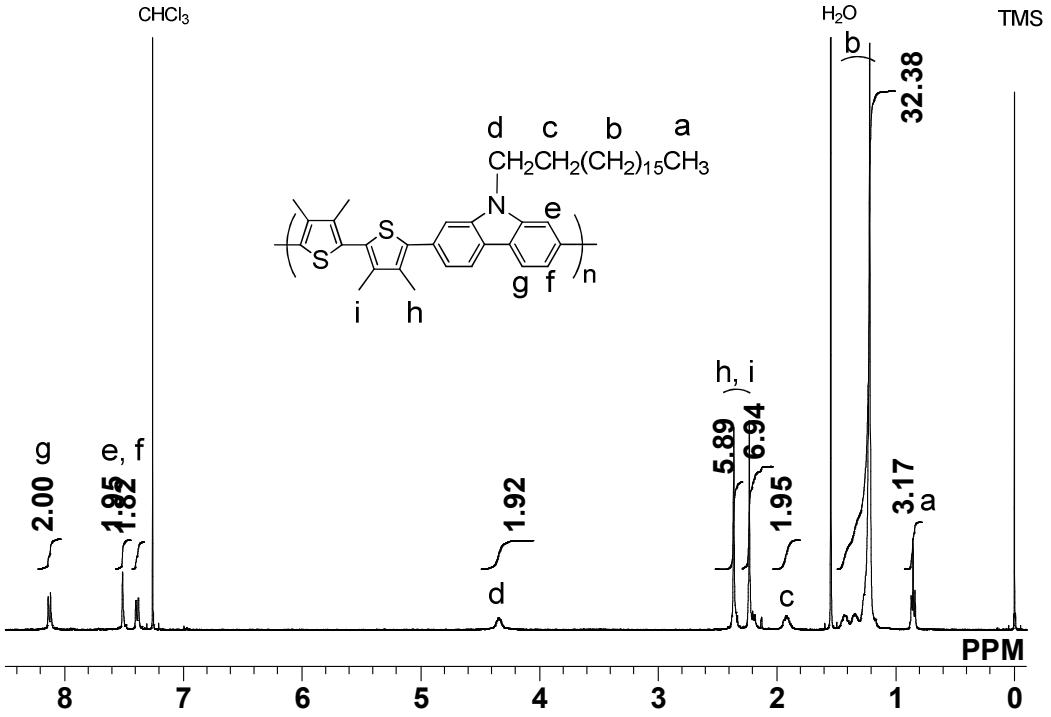


Figure S-7. ^{1}H NMR spectrum of **Polymer 2** (Table 1, Entry 4) (400 MHz, $CDCl_3$).

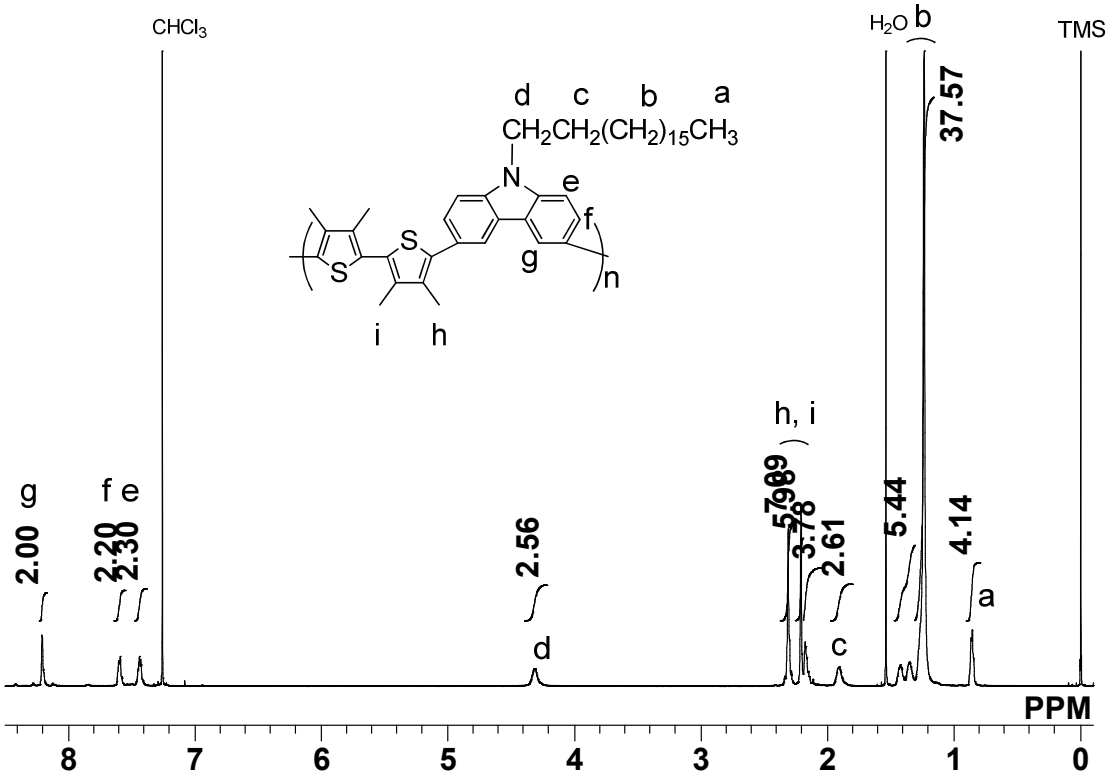


Figure S-8. ^{1}H NMR spectrum of **Polymer 3** (Table 1, Entry 6) (400 MHz, $CDCl_3$).

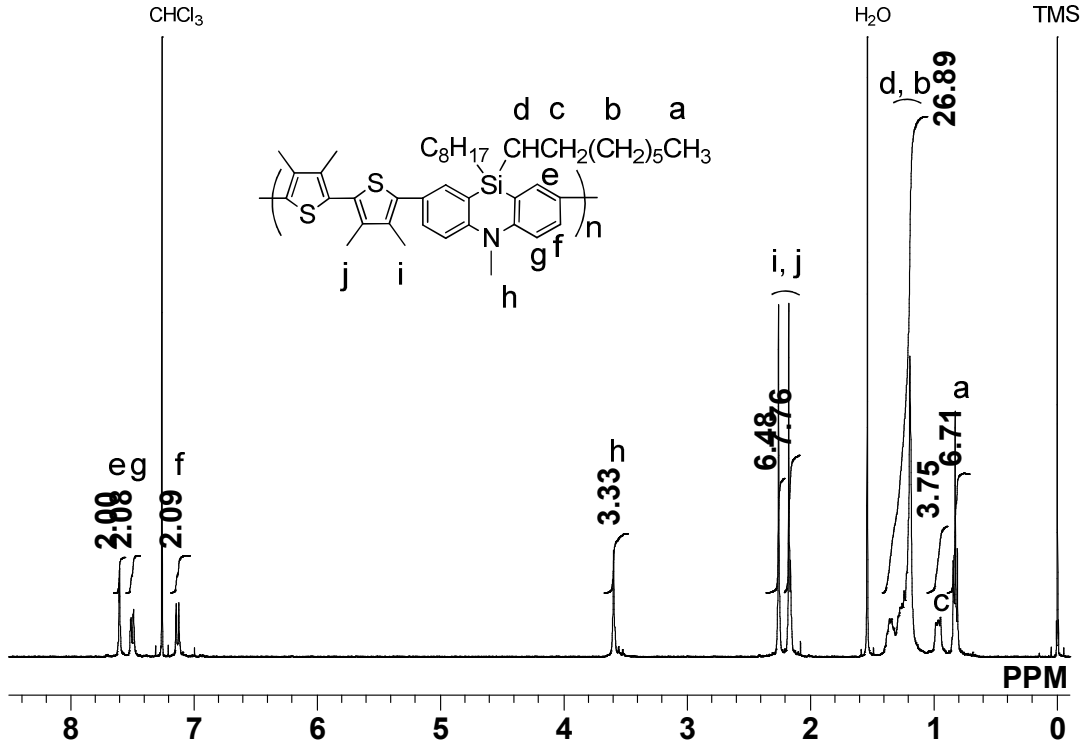


Figure S-9. ^{1}H NMR spectrum of **Polymer 4** (Table 1, Entry 8) (400 MHz, $CDCl_3$).

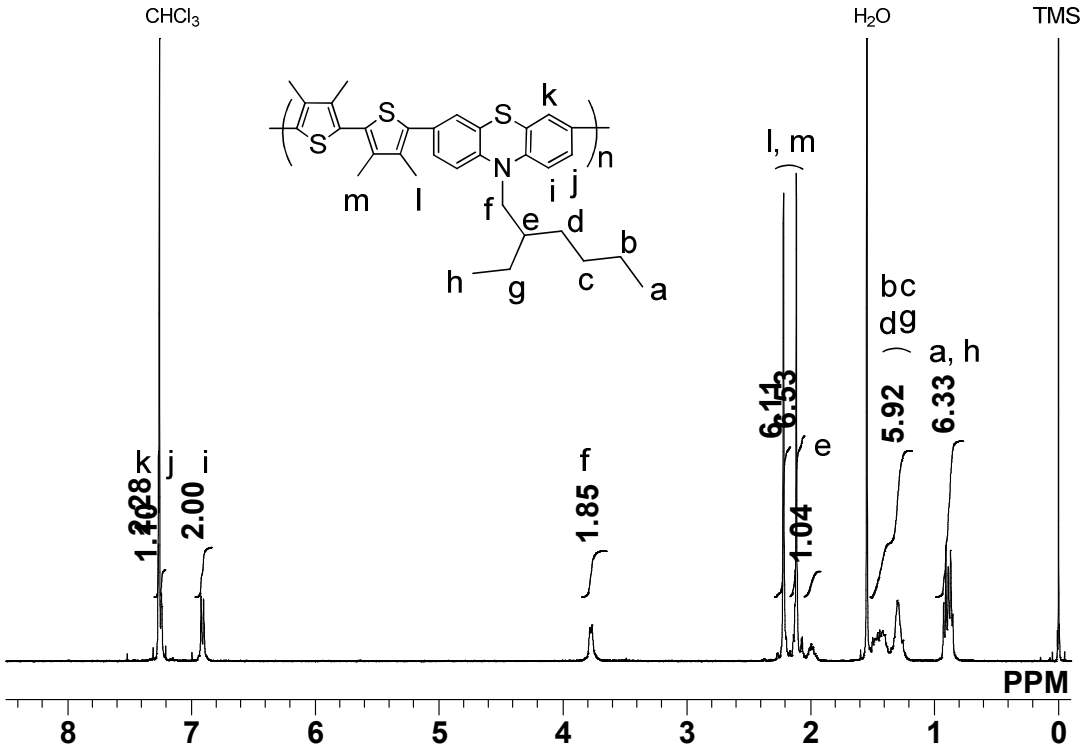


Figure S-10. ^{1}H NMR spectrum of **Polymer 5** (Table 1, Entry 10) (400 MHz, $CDCl_3$).

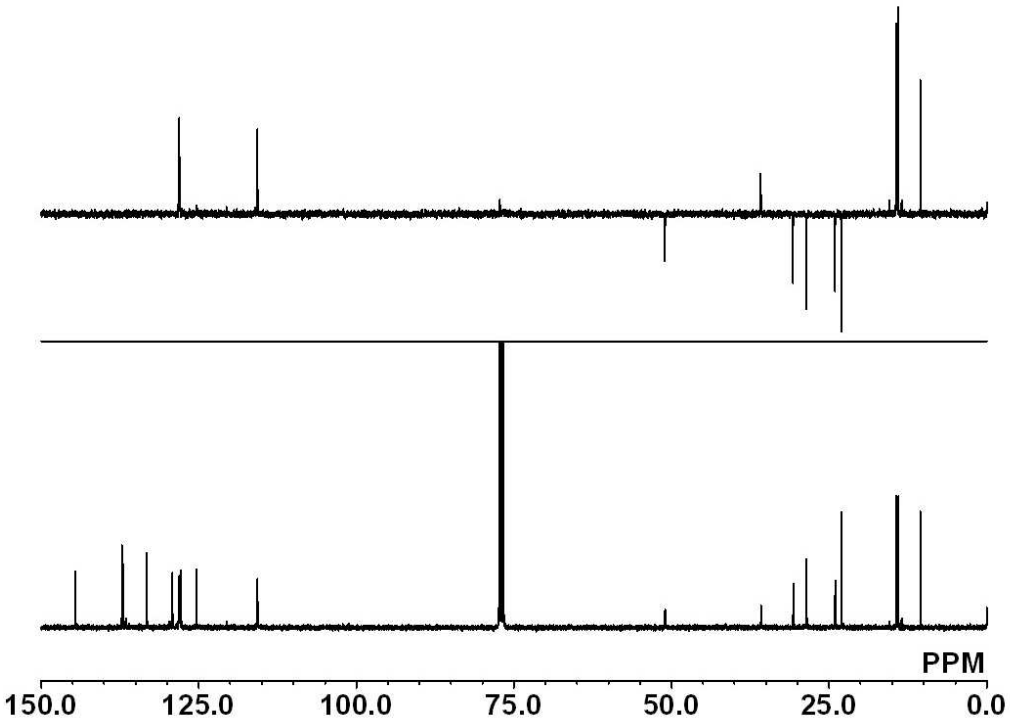


Figure S-11. (a) $^{13}C\{^{1}H\}$ and (b) DEPT 135 spectra of **Polymer 5** (Table 1, Entry 10) (125 MHz, $CDCl_3$).

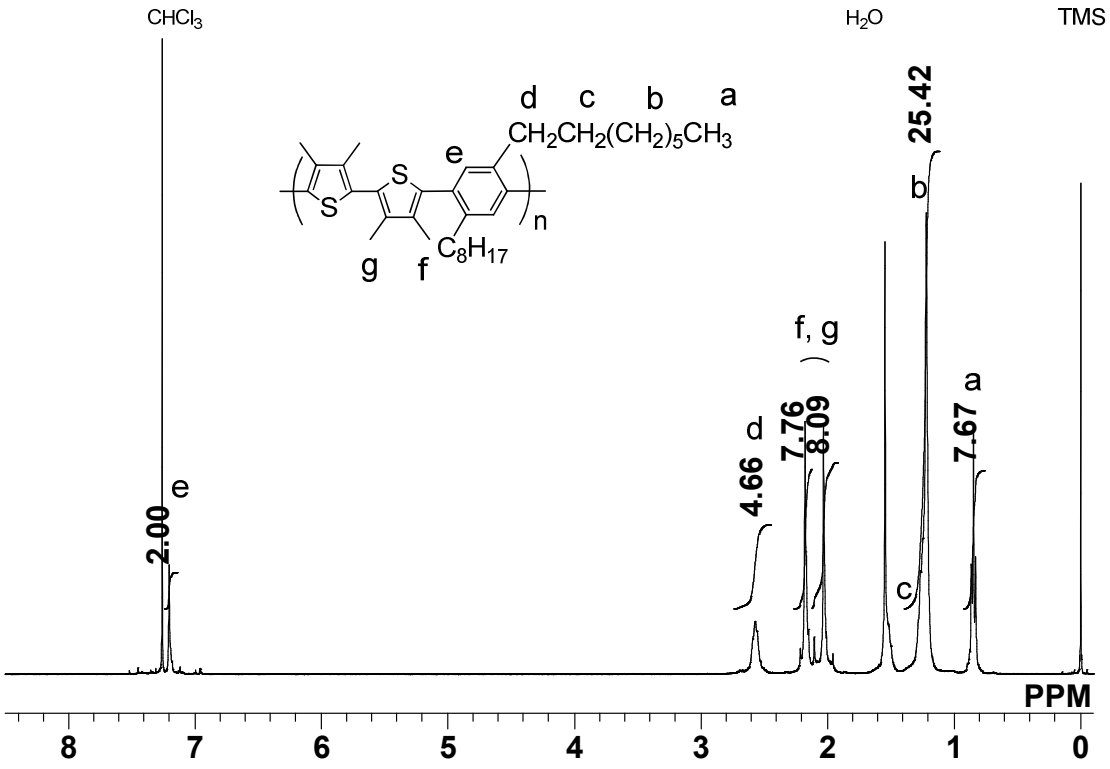


Figure S-12. ^{1}H NMR spectrum of **Polymer 6** (Table 1, Entry 12) (400 MHz, $CDCl_3$).

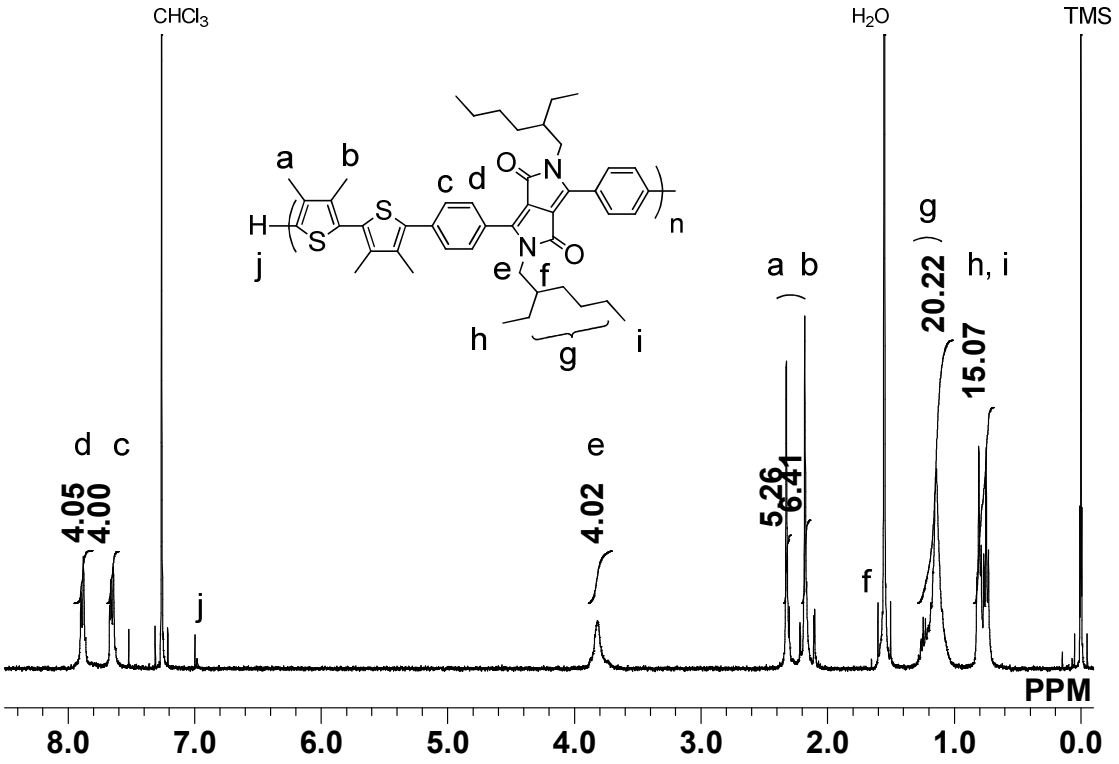


Figure S-13. ^{1}H NMR spectrum of **Polymer 7** (Table 1, Entry 13) (400 MHz, $CDCl_3$).

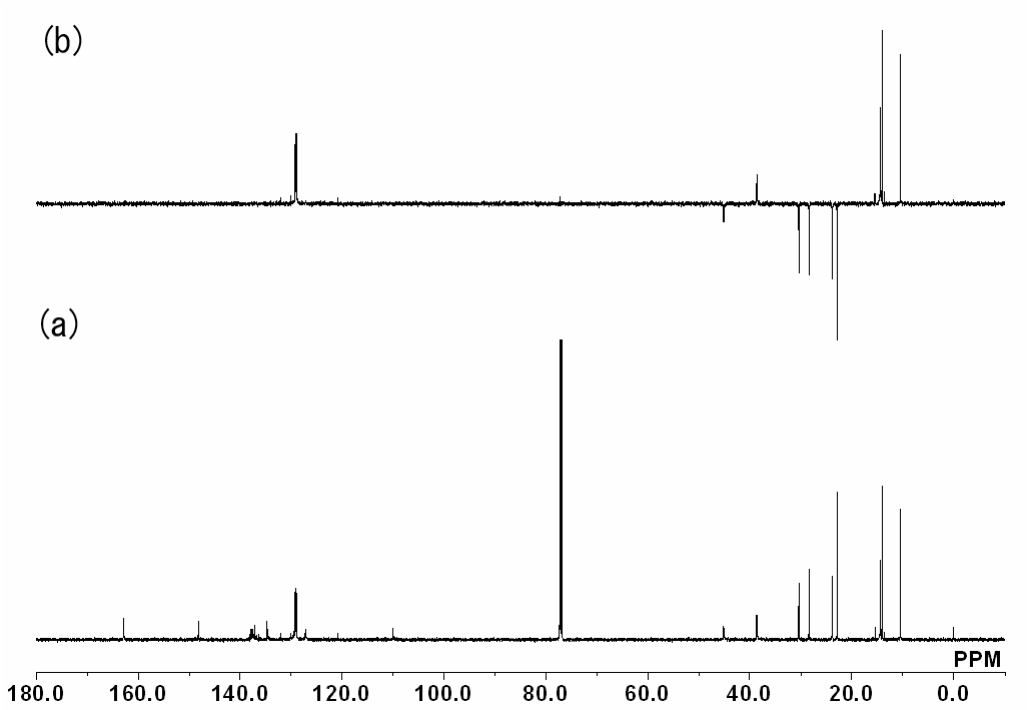


Figure S-14. (a) ^{13}C{^{1}H} and (b) DEPT 135 spectra of **Polymer 7** (Table 1, Entry 13) (125 MHz, $CDCl_3$).

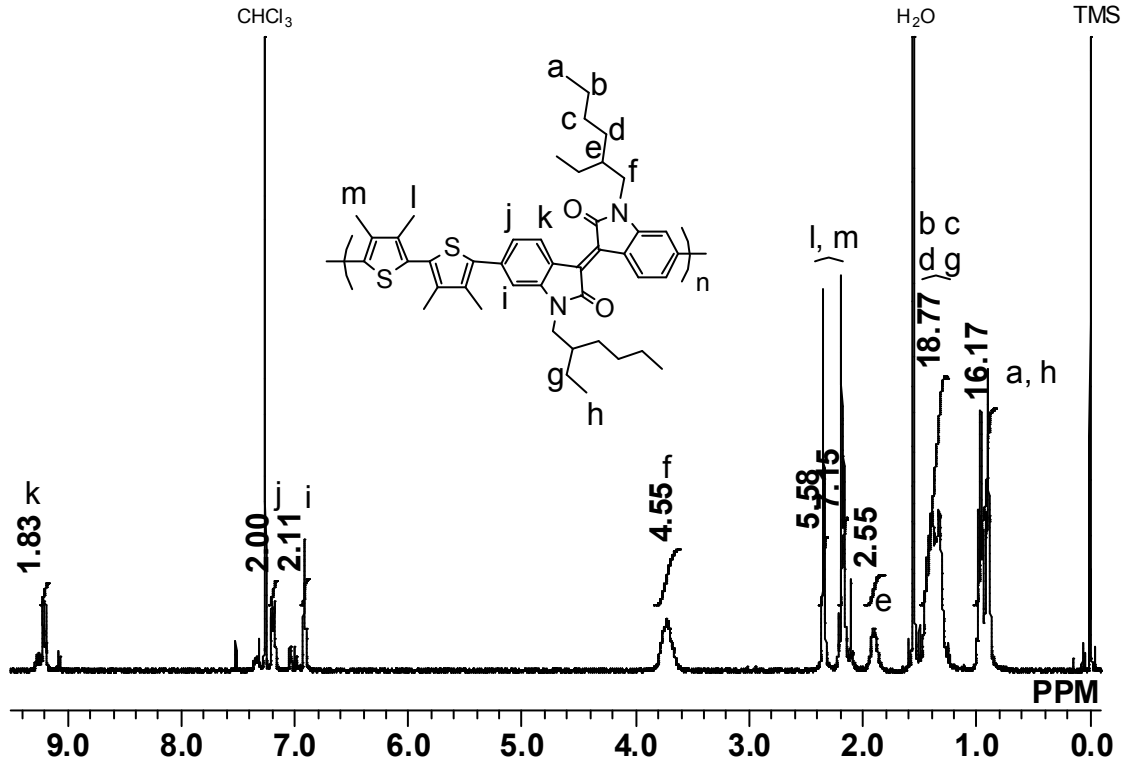


Figure S-15. ^{1}H NMR spectrum of **Polymer 8** (Table 1, Entry 14) (400 MHz, $CDCl_3$).

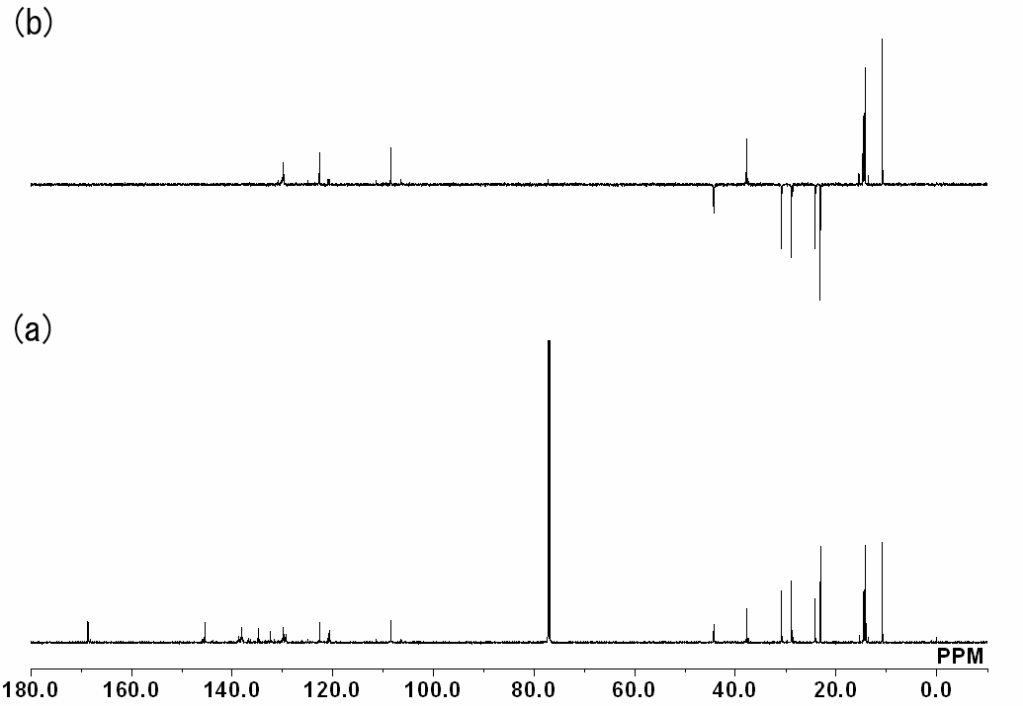


Figure S-16. (a) $^{13}C\{^{1}H\}$ and (b) DEPT 135 spectra of **Polymer 8** (Table 1, Entry 14) (100 MHz, $CDCl_3$).