Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information for

Synthesis of 4,4'-Dinonyl-2,2'-bithiazole-base Copolymers via Pd-Catalyzed Direct C−H Arylation

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Experimental Section

1. Materials

2,7-dibromo-9,9-dioctylfluorene, 1,4-dibromo-2,5-difluorobenzene, 1,4-dibromo-2,5-dioctylbenzene, 1,4-dibromobenzene, 4,4'-dibromobiphenyl, $Pd(OAc)_2$, $PCy_3 \cdot HBF_4$, pivalic acid (PivOH), K_2CO_3, and other chemicals were received from commercial suppliers and used without further purification. Anhydrous dimethylacetamide (DMAc) were purchased from Kanto Chemical and used as a dry solvent. 4,4'-dinonyl-2,2'-bithiazole was prepared according to the literature methods.[1] ! 4,4'-Dinonyl-2,2'-bithiazole in higgly pure form was obtained as needle-shaped crystals by further purification through Medium Pressure Liquid Chromatography (MPLC) and crystallization..

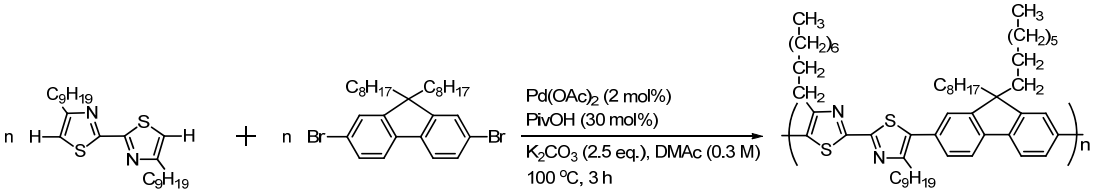
Reference

1 W.-Y. Wong, X.-Z. Wang, Z. He, K.-K. Chan, A. B. Djurišić, K.-Y. Cheung, C.-T. Yip, A. M.-C. Ng, Y.-Y. Xi, C. S.-K. Mak and W.-K. Chan, *J. Am. Chem. Soc.*, 2007, **129**, 14372.

2. General Methods:

NMR spectra were recorded on a Bruker AVANCE-400 NMR spectrometer and a JEOL JNM-ECS-400 NMR spectrometer. ^{1}H and $^{13}C\{^{1}H\}$ spectra were measured with tetramethylsilane (TMS) as internal standard. ^{19}F NMR spectra were measured with hexafluorobenzene as external standard (-162.9 ppm). Gel permeation chromatography (GPC) measurements were carried out on a SHIMADZU prominence GPC system equipped with polystyrene gel columns, using $CHCl_3$ as an eluent after calibration with polystyrene standards. MALDI-TOF-MS spectra were recorded on AB SCIEX MALDI TOF/TOF 5800 using dithranol as a matrix. All manipulations for the reactions were carried out under nitrogen atmosphere using a standard Schlenk technique. Column chromatography was carried out with silica gel 60 (Kanto, 40-100 μm, neutral). Purification by MPLC was carried out on a YAMAZEN FR50N using EtOAc / hexane (1:50 v/v) as an eluent.

3. Typical polycondensation of 4,4'-dinonyl-2,2'-bithiazole with 2,7-dibromo-9,9-dioctylfluorene under the optimized conditions (Table 1, Entry 4)

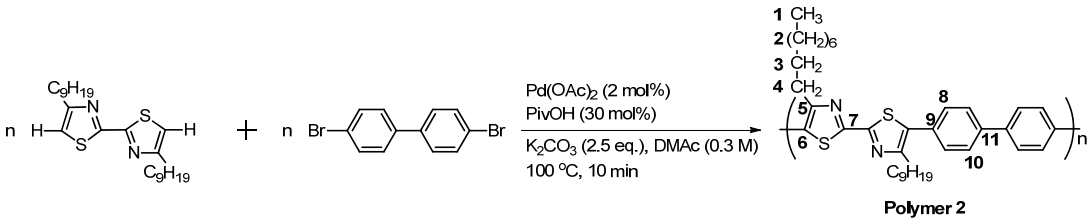


Polymer 1

Polymer 1 was obtained by the typical procedure in Experimental Part.

The polycondensation reactions of 4,4'-dinonyl-2,2'-bithiazole with 2,7-dibromo-9,9-dioctylfluorene in the presence of phosphine ligand were carried out for 3 h and 12 h respectively according to the typical polycondensation procedure except for using $PCy_3 \cdot HBF_4$ (18.4 mg, 0.050 mmol).

4. Polycondensation of 4,4'-dinonyl-2,2'-bithiazole with 4,4'-dibromobiphenyl (for 10 min, Table 2, Entry 2)

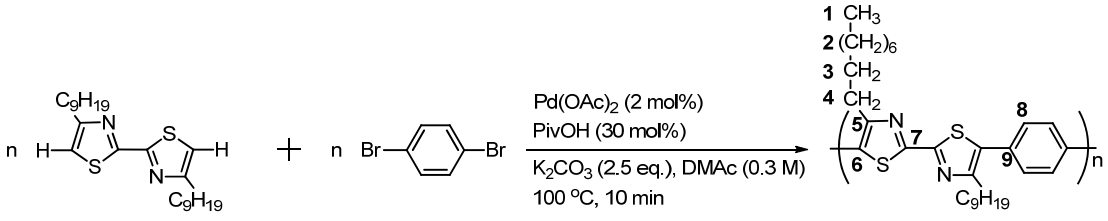


Polymer 2

The polycondensation reaction of 4,4'-dinonyl-2,2'-bithiazole (210 mg, 0.50 mmol) with 4,4'-dibromobiphenyl (156 mg, 0.50 mmol) was carried out for 10 min. **Polymer 2** was obtained by the method according to the typical polycondensation procedure as orange-yellow solid in 87% yield. M_n = 10000, M_w/M_n = 1.25. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 7.75 (4H, d, J = 8.0 Hz, H^8), 7.60 (4H, d, J = 8.0 Hz, H^{10}), 2.88 (4H, br, H^4), 1.80 (4H, br, H^3), 1.31 (24H, br, H^2), 0.87 (6H, br, H^1). ^{13}C{^{1}H} NMR (100 MHz, $Cl_2CDCDCl_2$, 353 K): δ 159.0 (C^7), 154.6 (C^6), 140.0 (C^{11}), 133.9 (C^5), 131.7 (C^9), 130.1 (C^8), 127.5 (C^{10}), 32.1 (CH_2), 30.1 (CH_2), 30.0-29.3 (5×CH_2), 22.8 (CH_2), 14.3 (CH_3).

The same reaction was also carried out for 3 h to give **Polymer 2!**) (M_n = 14700, M_w/M_n = 2.6) in 70% yield and insoluble products (**Table 2, Entry 1**).

5. Polycondensation of 4,4'-dinonyl-2,2'-bithiazole with 1,4-dibromobenzene (for 10 min, Table 2, Entry 4)



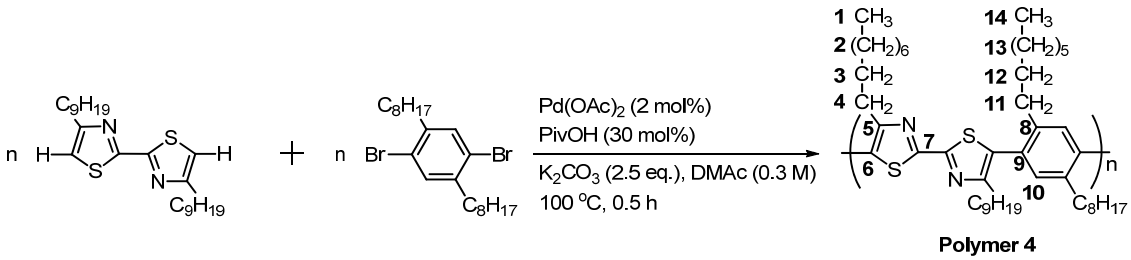
Polymer 3

The polycondensation reaction of 4,4'-dinonyl-2,2'-bithiazole (210 mg, 0.50 mmol) with 1,4-dibromobenzene (118 mg, 0.50 mmol) was carried out for 10 min. **Polymer 3** was obtained by the method according to the typical polycondensation procedure as orange-yellow solid in 16% yield. M_n = 4300, M_w/M_n = 1.16. ^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$, 353 K):

δ 7.56 (4H, d, J = 6.4 Hz, H^8), 2.87 (4H, br, H^4), 1.80 (4H, br, H^3), 1.32 (24H, br, H^2), 0.88 (6H, br, H^1). $^{13}C\{^1H\}$ NMR (100 MHz, $Cl_2CDCDCl_2$, 353 K): δ 159.1 (C^7), 154.8 (C^6), 133.6 (C^5), 132.1 (C^9), 129.9 (C^8), 32.1 (CH_2), 30.1 (CH_2), 30.0-29.3 ($5\times CH_2$), 22.8 (CH_2), 14.3 (CH_3). In addition to **Polymer 3**, the polycondensation for 10 min simultaneously gave insoluble products.

The same reaction was also carried out for 3 h to give **Polymer 3** (M_n = 5300, M_w/M_n = 1.29) in 10% yield and insoluble products (**Table 2, Entry 3)**.

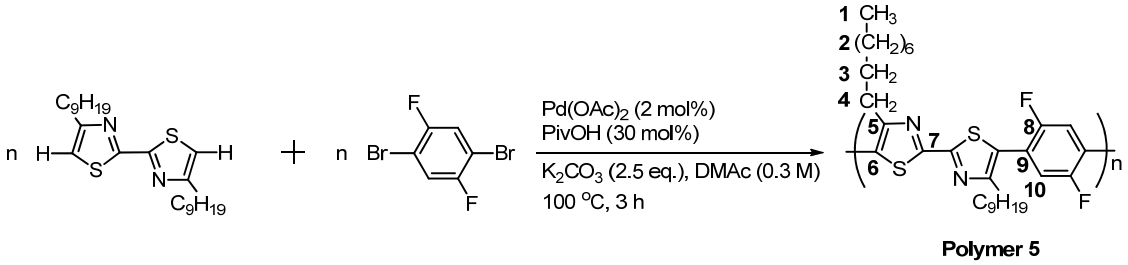
6. Polycondensation of 4,4'-dinonyl-2,2'-bithiazole with 1,4-dibromo-2,5-dioctylbenzene (for 0.5 h, Table 2, Entry 6)



The polycondensation reaction of 4,4'-dinonyl-2,2'-bithiazole (210 mg, 0.50 mmol) with 1,4-dibromo-2,5-dioctylbenzene (230 mg, 0.50 mmol) was carried out for 0.5 h. **Polymer 4** was obtained as yellow solid in 93% yield by the method according to the typical polycondensation procedure except for the purification step. In this case, washing with hexane was omitted because **Polymer 4** was soluble in hexane. M_n = 15300, M_w/M_n = 1.63. ^1H NMR (400 MHz, $Cl_2CDCDCl_2$, 293 K): δ 7.18 (2H, br, H^{10}), 2.59 (8H, br, H^4, H^{11}), 1.69 (4H, br, H^3), 1.49 (4H, br, H^{12}), 1.24 (44H, br, H^2, H^{13}), 0.82 (12H, br, H^1, H^{14}). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ 159.7 (C^7), 155.4 (C^6), 140.0 (C^5), 132.5 (C^{10}), 131.9 (C^8 or C^9), 131.0 (C^8 or C^9), 32.8 (CH_2), 32.0 (CH_2), 31.9 (CH_2), 30.9 (CH_2), 30.0-29.0 ($9\times CH_2$), 22.7 ($2\times CH_2$), 14.1 ($2\times CH_3$).

The same reaction was also carried out for 3 h to give **Polymer 4 (**M_n = 35900, M_w/M_n = 2.89) in 46% yield and insoluble products (**Table 2, Entry 5)**.

7. Polycondensation of 4,4'-dinonyl-2,2'-bithiazole with 1,4-dibromo-2,5-difluorobenzene (Table 2, Entry 7)



Polymer 5

The polycondensation reaction of 4,4'-dinonyl-2,2'-bithiazole (210 mg, 0.50 mmol) with 1,4-dibromo-2,5-difluorobenzene (136 mg, 0.50 mmol) was carried out for 3 h. **Polymer 5** was obtained by the method according to the typical polycondensation procedure as orange solid in 93% yield. M_n = 13000, M_w/M_n = 4.45 (bimodal). ^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$, 293 K): δ 7.25 (2H, br, H^{10}), 2.72 (4H, br, H^4), 1.76 (4H, br, H^3), 1.22 (24H, br, H^2), 0.82 (6H, br, H^1). $^{13}C\{^1H\}$ NMR (100 MHz, $Cl_2CDCDCl_2$, 333 K): δ 160.8 (C^7), 157.5 (C^6), 155.7 (dd, J_{C-F} = 3,6, 247.2 Hz, C^8), 125.2 (C^5), 121.7 (dd, J_{C-F} = 12.4, 12.4 Hz, C^9), 119.2 (m, C^{10}), 32.1 (CH_2), 30.2 (CH_2), 29.9-29.0 (5×CH_2), 22.8 (CH_2), 14.2 (CH_3). ^{19}F NMR (377 MHz, $Cl_2CDCDCl_2$, 293K): δ -113.05, -113.12/ The integral ratio of the two signals was 1:1. The two separated signals are probably due to the existence of rotamers because the steric hindrance of F atom is likely to block the free rotation of the aromatic rings in **Polymer 5**.

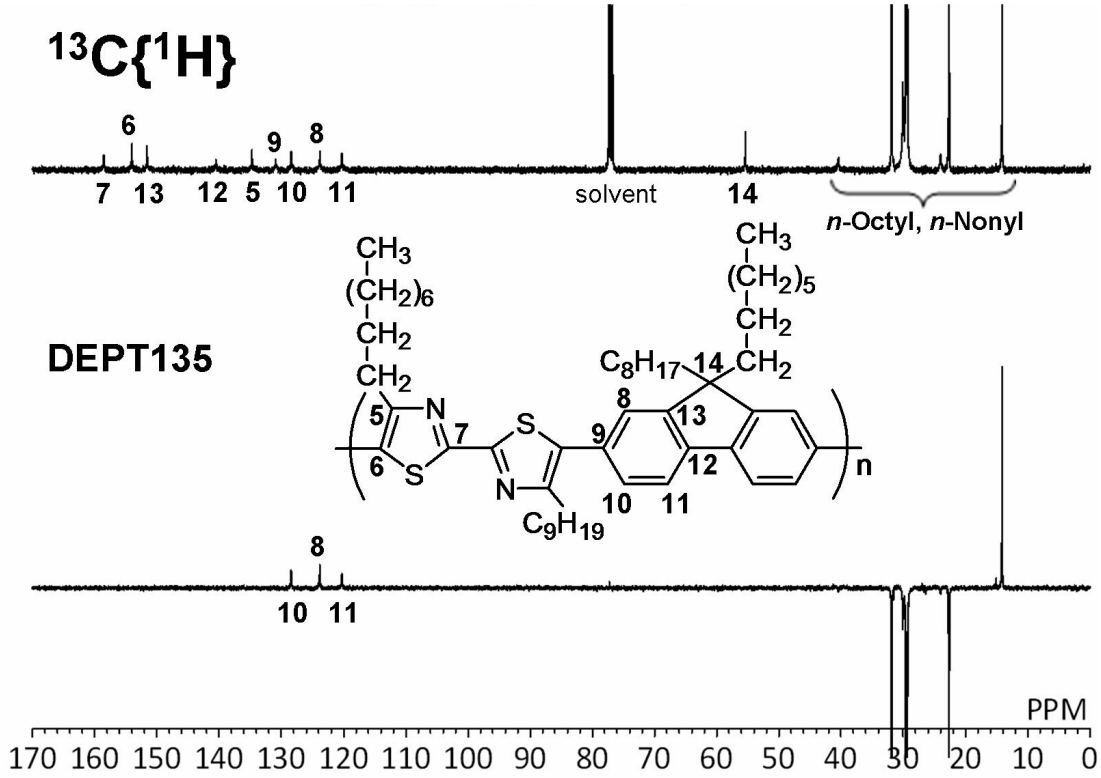


Figure S-1. $^{13}C\{^{1}H\}$ and DEPT NMR spectra of **Polymer 1** (Table 1, Entry 4) (100 MHz, $CDCl_3$, 293 K).

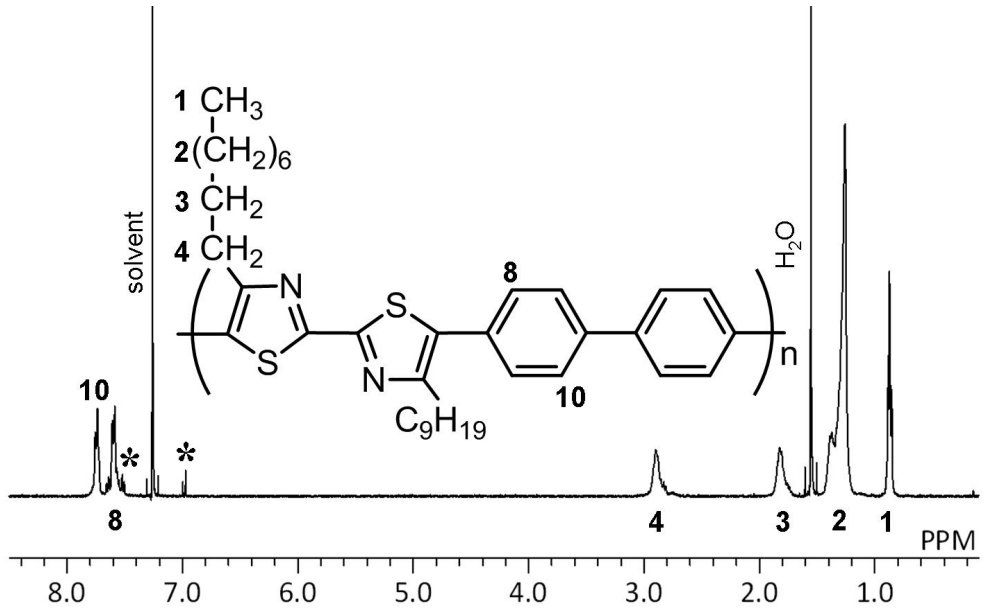


Figure S-2. ^{1}H NMR spectrum of **Polymer 2** (Table 2, Entry 2) (400 MHz, $CDCl_3$, 293 K). The signals with an asterisk correspond to the protons of the terminal 4,4'-dinonyl-5H-5-2,2'-bithiazole units (7.0 ppm) and 4'-bromo-4-biphenyl units (7.5, 7.6 ppm) of **Polymer 2**.

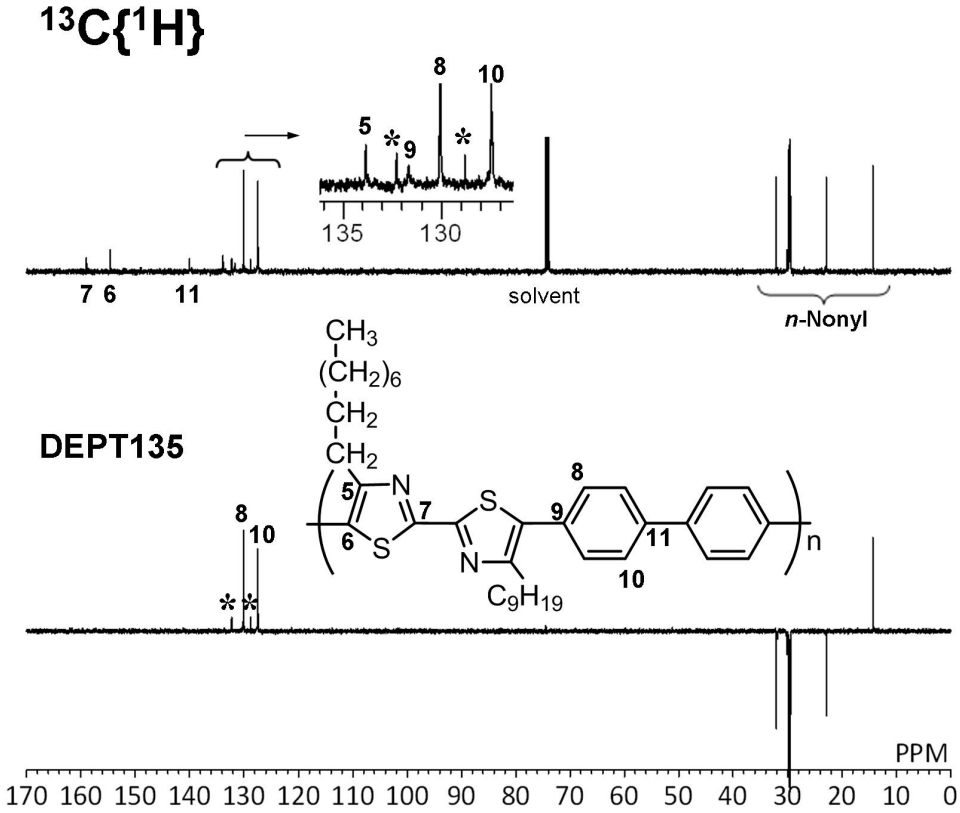


Figure S-3. $^{13}C\{^{1}H\}$ and DEPT NMR spectra of **Polymer 2** (Table 2, Entry 2) (100 MHz, $Cl_2CDCDCl_2$, 353 K). The signals with an asterisk correspond to the protons of the terminal units of **Polymer 2**.

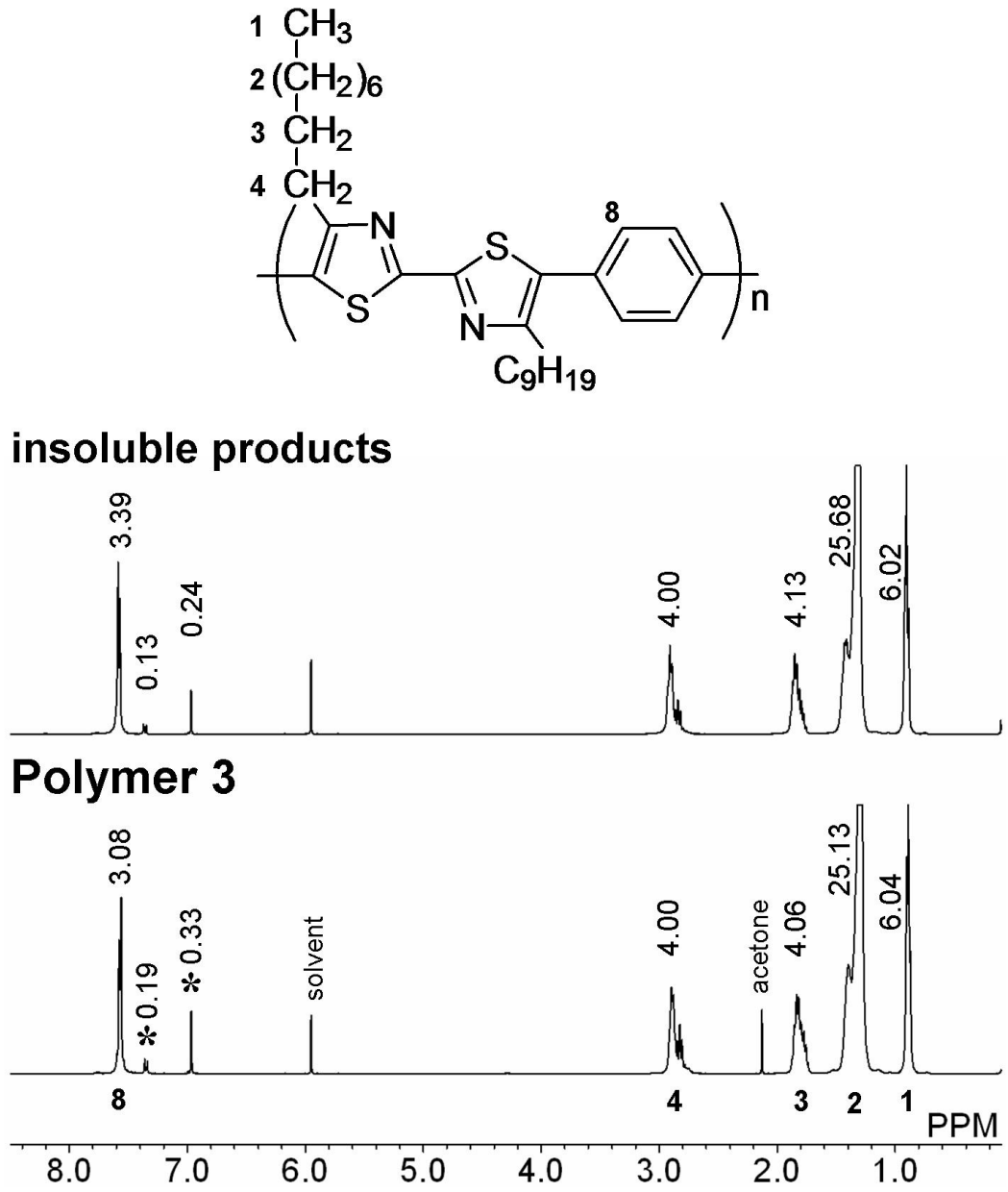


Figure S-4. ^{1}H NMR spectra of **Polymer 3** and insoluble products in $CHCl_3$ (Table 2, Entry 4) (400 MHz, $Cl_2CDCDCl_2$, 353 K). The signals with an asterisk correspond to the protons of the terminal 4,4'-dinonyl-5H-5-2,2'-bithiazole units (7.0 ppm) and 4-bromo-1-phenyl units (7.4 ppm) of **Polymer 3**.

Comments:

In the ^{1}H NMR spectra of **Polymer 3**, the integral values of the protons at the 8 positions were 3.08 and 3.39 and the insoluble products, respectively. These values were significantly smaller than their theoretical value (4.00) calculated according to the linear structure. The reduction of the protons at the 8 positions indicates the existence of branching structures at the 8 positions caused by side reactions,.

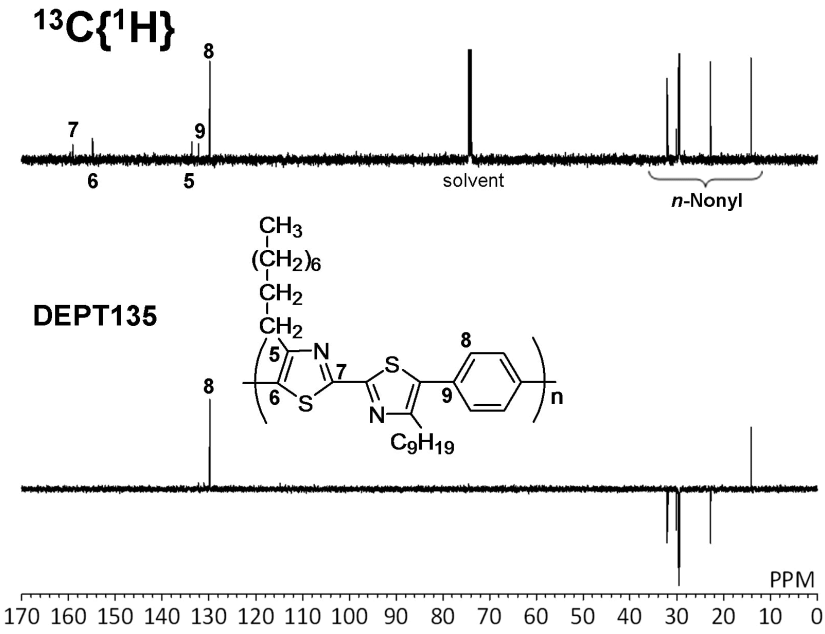


Figure S-5. $^{13}C\{^{1}H\}$ and DEPT NMR spectra of the insoluble products in $CHCl_3$ from the reaction of entry 4 in Table 2. (100 MHz, $Cl_2CDCDCl_2$, 353 K).

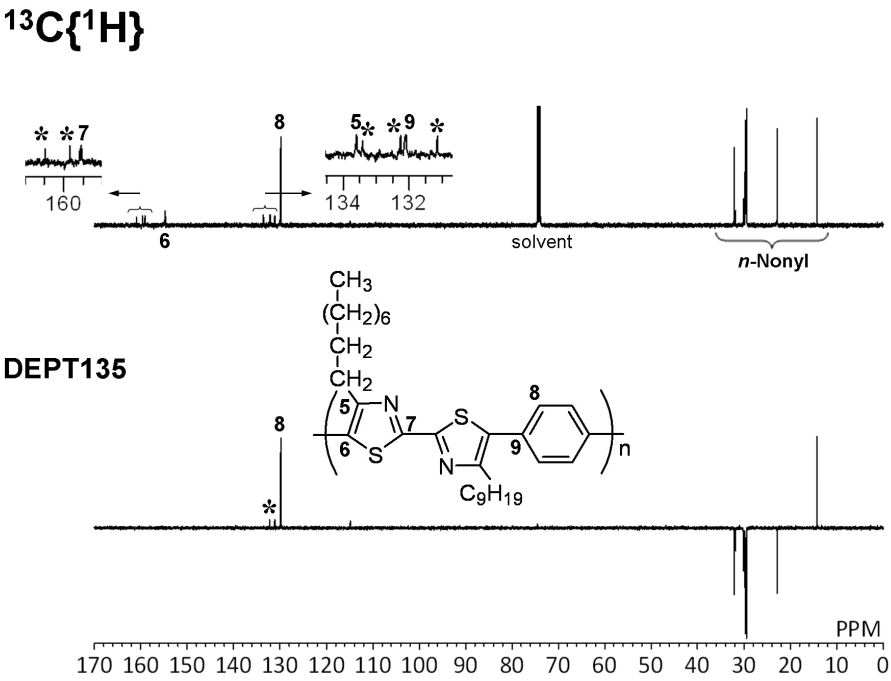


Figure S-6. $^{13}C\{^{1}H\}$ and DEPT NMR spectra of **Polymer 3** from the reaction of entry 4 in Table 2 (100 MHz, $Cl_2CDCDCl_2$, 353 K). The signals with an asterisk correspond to the protons of the terminal units.

Comments:

The insoluble products in $CHCl_3$ gave a relatively simple $^{13}C\{^{1}H\}$ spectrum (Figure S-5) compared to the soluble fraction of the product, **Polymer 3** (Figure S-6) probably due to the high molecular weight of the product.

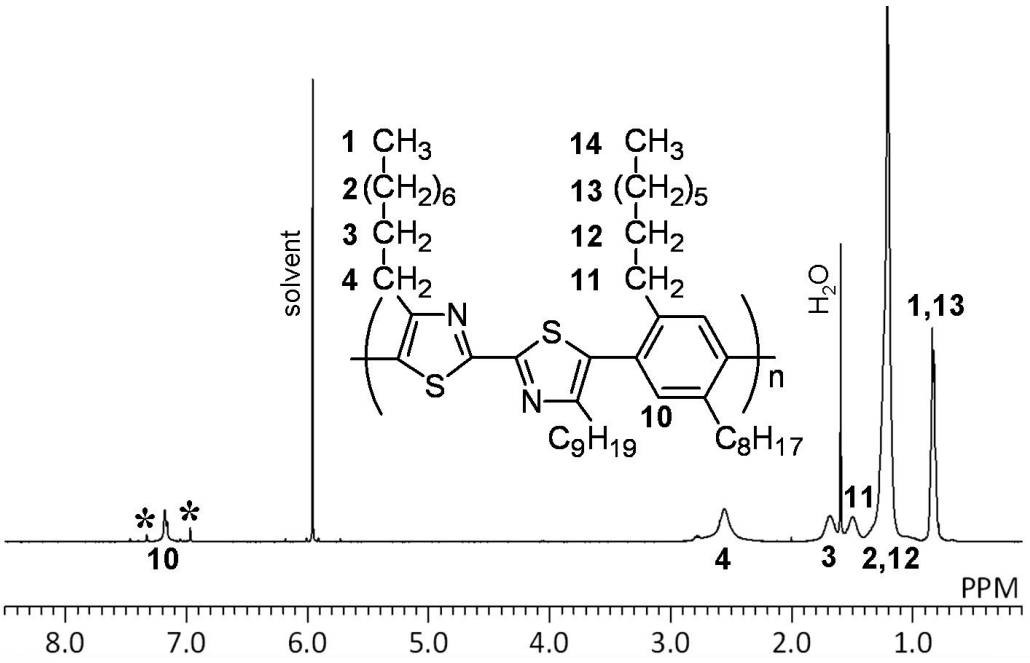


Figure S-7. ^{1}H NMR spectrum of **Polymer 4** (Table 2, Entry 6) (400 MHz, $Cl_2CDCDCl_2$, 293 K). The signals with an asterisk correspond to the protons of the terminal 4,4'-dinonyl-5H-5-2,2'-bithiazole unit (7.0 ppm) and 4-bromo-2,5-dioctyl-1-phenyl units (7.3 ppm) of **Polymer 4**.

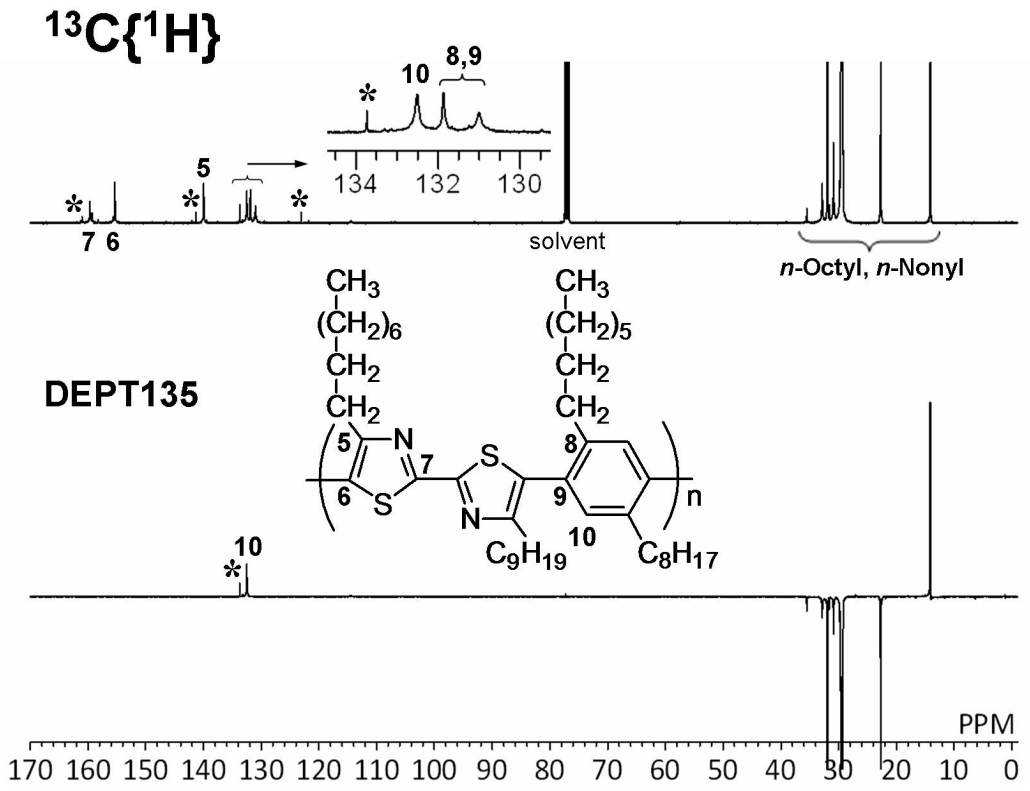


Figure S-8. ^{13}C{^{1}H} and DEPT NMR spectra of **Polymer 4** (Table 2, Entry 6) (100 MHz, $CDCl_3$, 293 K). The signals with an asterisk correspond to the carbons of the terminal units of **Polymer 4**.

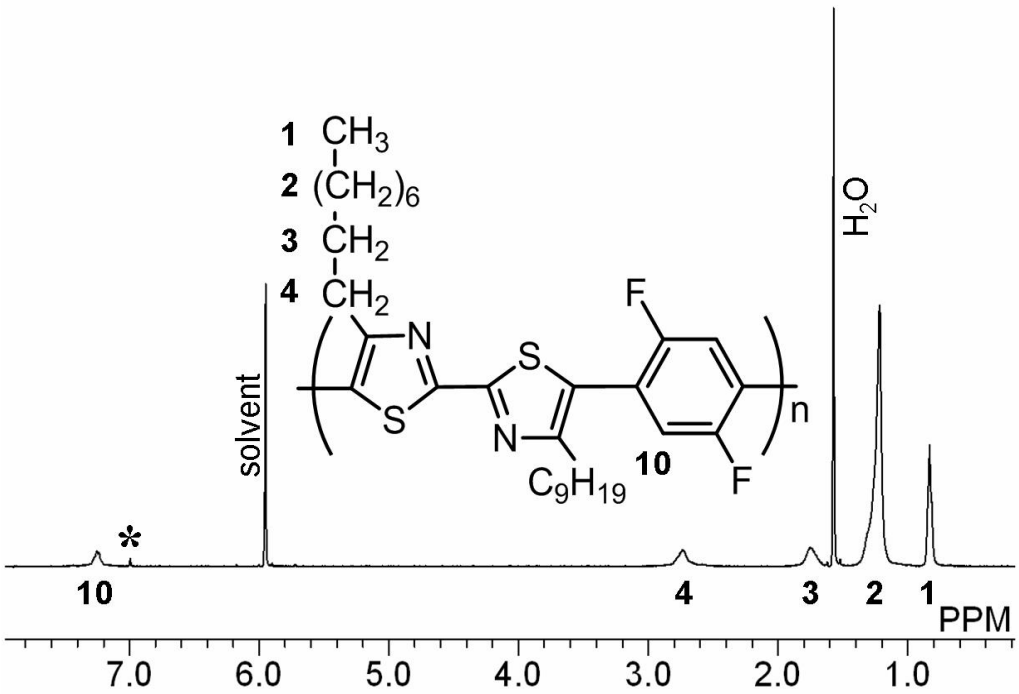


Figure S-9. ^{1}H NMR spectrum of **Polymer 5** (Table 2, Entry 7) (400 MHz, $Cl_2CDCDCl_2$, 293 K). The two signals with an asterisk correspond to the protons of the terminal 4,4'-dinonyl-5H-5-2,2'-bithiazole units (7.0 ppm).

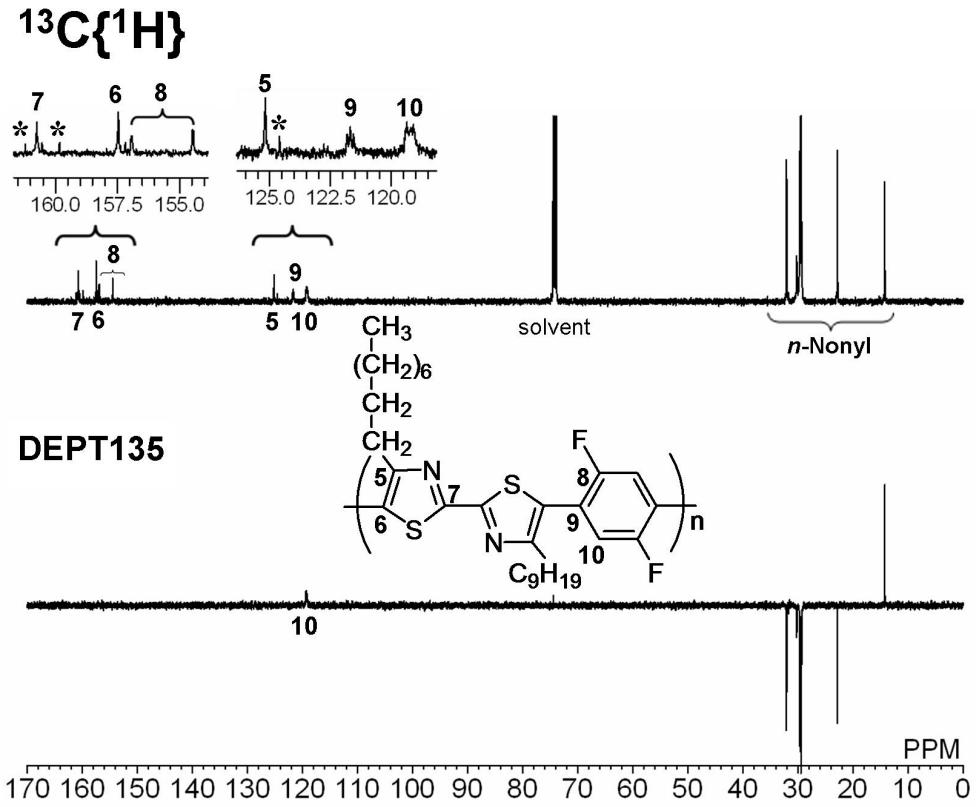


Figure S-10. $^{13}C\{^{1}H\}$ and DEPT NMR spectra of **Polymer 5** (Table 2, Entry 7) (100 MHz, $Cl_2CDCDCl_2$, 333 K). The signals with an asterisk correspond to the carbons of the terminal units of **Polymer 5**.

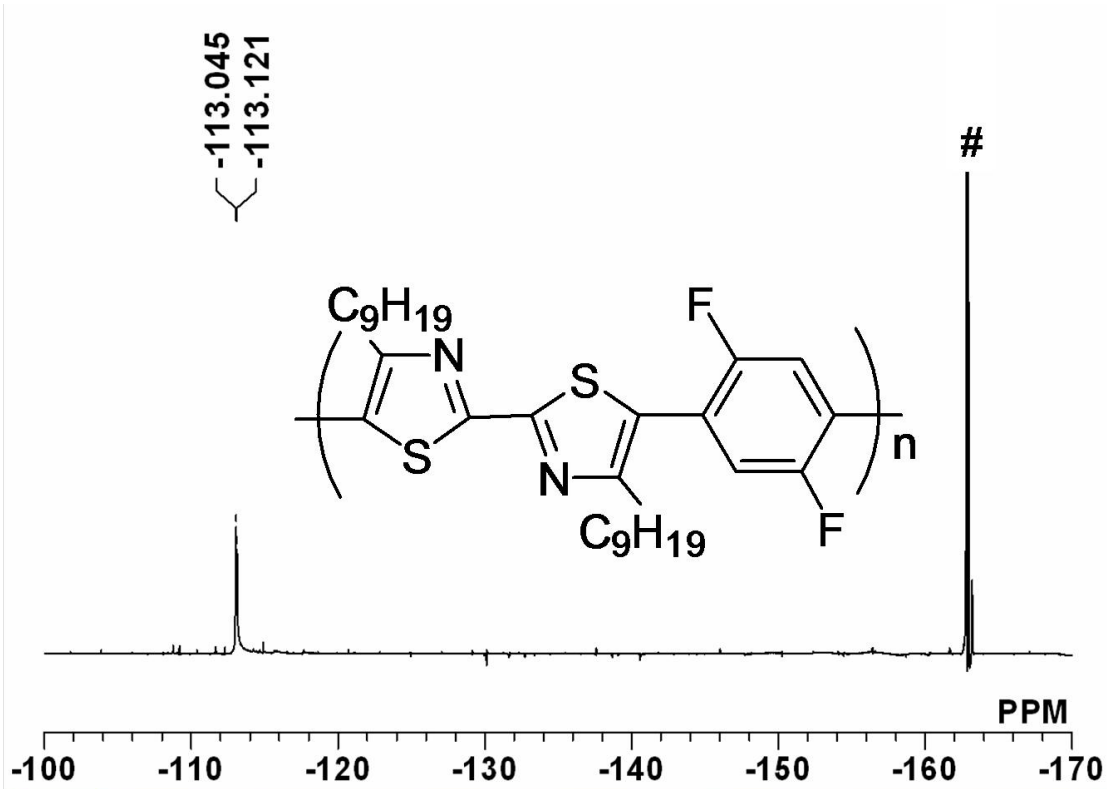


Figure S-11. ^{19}F NMR spectrum of **Polymer 5** (Table 2, Entry 7) (377 MHz, $Cl_2CDCDCl_2$, 293 K). The signal with a pound corresponds to hexafluorobenzene as an internal standard (-162.9 ppm).

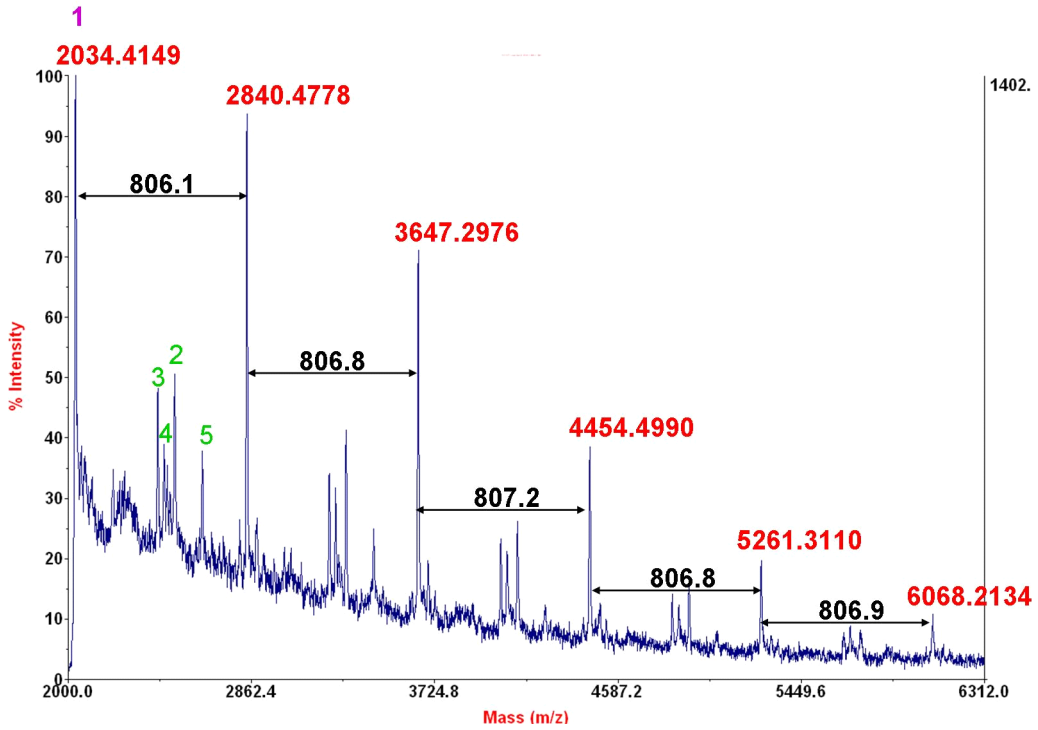
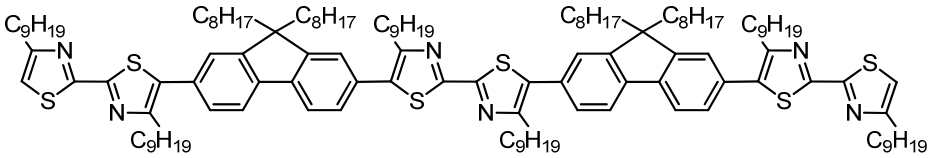


Figure S-12. Positive ion MALDI-TOF-MASS spectrum of **Polymer 1** (Table 1, Entry 4) using dithranol as a matrix and des-Arg^1-Bradykinin, Anglotensin I and Glu^1-Flibrinopeptide B as external standards.

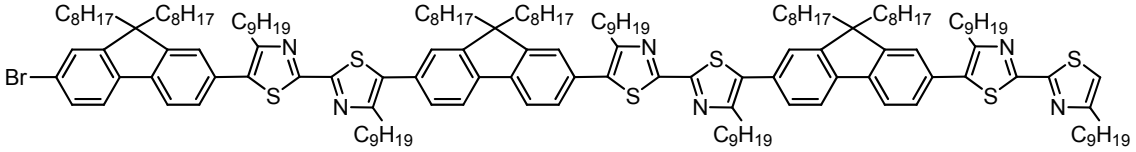
Calculated mass for the repeating unit: **806**

Peak 1, Found m/z : **2034.4149**



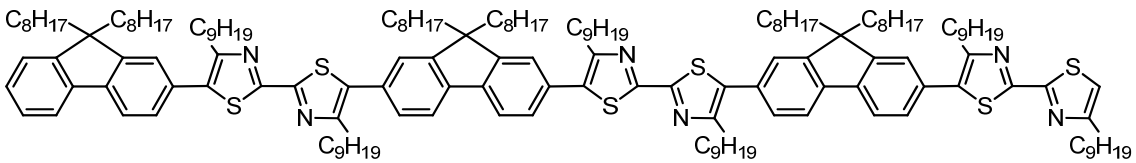
Calculated mass for H-($C_{53}H_{78}N_2S_2$)$_2$-($C_{24}H_{38}N_2S_2$)-H : **2034.38792**

Peak 2, Found m/z : **2500.8171**



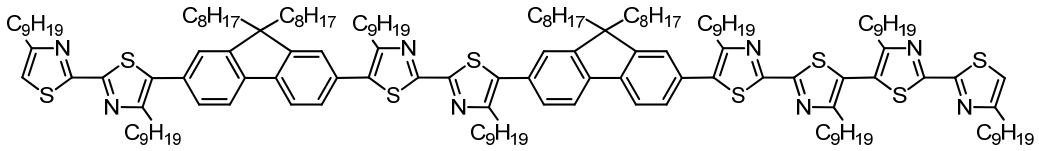
Calculated mass for Br-($C_{53}H_{78}N_2S_2$)$_3$-H : **2500.61143**

Peak 3, Found m/z : **2421.9512**



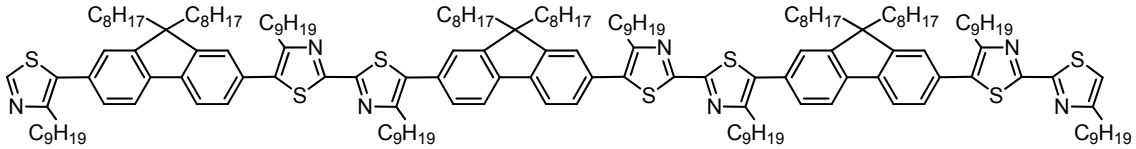
Calculated mass for H-($C_{53}H_{78}N_2S_2$)$_3$-H : **2422.70092**

Peak 4, Found m/z : **2451.6040**



Calculated mass for H-$(C_{24}H_{38}N_2S_2)_2$-$(C_{53}H_{78}N_2S_2)_2$-H : **2452.63556**

Peak 5, Found m/z : **2631.0215**



Calculated mass for H-$(C_{12}H_{19}NS)$-$(C_{53}H_{78}N_2S_2)_3$-H : **2631.82474**

Comments:

The MALDI-TOF-MASS spectrum of **Polymer 1** exhibited the mass of the repeating unit! (806), which is in accordance with the calculated mass of a unit of (4,4'-dinonyl-2,2'-bithiazole-5,5'-diyl)-(9,9-dioctylfluorene-2,7-diyl). The main peaks (peak 1) correspond to the alternating structure of the **Polymer 1** with two 4,4'-dinonyl-5H-2,2'-bithiazole terminals. In addition, the minor peaks such as peak 2 and 3 correspond to the structures with other terminals such as a fluorine unit (see Figure S-13 in supporting information).!!The peak with m/z of 2451.604 (peak 4) corresponding to the alternating structure with an extra bithiazole unit was observed in low intensity, which indicated a side reaction was minor.

In addition, the similar structures having an extra bithiazole unit were also observed in the MALDI-TOF-MASS spectra of **Polymer 2**, **3**, **4**, **5** with weak intensity (see Peak 5 in Figure S-13, Peak 6 in Figure S-14, Peak 3, 6 in Figure S-15 and Peak 3 in Figure S-16).

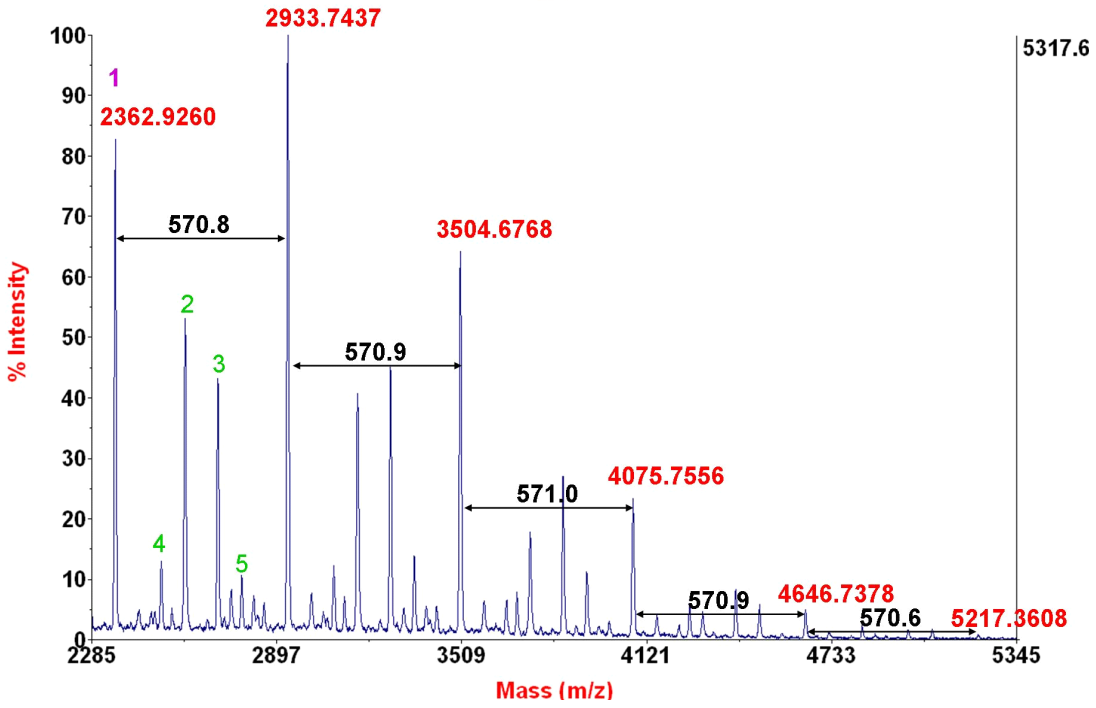
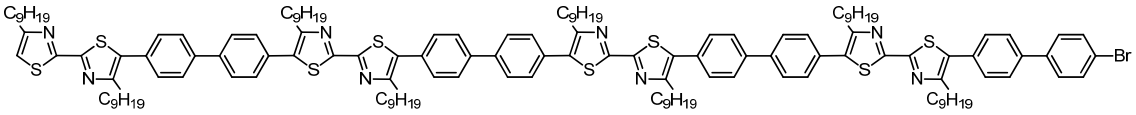


Figure S-13. Positive ion MALDI-TOF-MASS spectrum of **Polymer 2** (Table 2, Entry 2) using dithranol as a matrix and des-Arg^1-Bradykinin, Anglotensin I and Glu^1-Flibrinopeptide B as external standards.

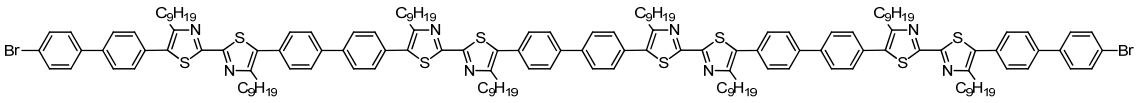
Calculated mass for the repeating unit: **570**

Peak 1, Found m/z : **2362.9260**



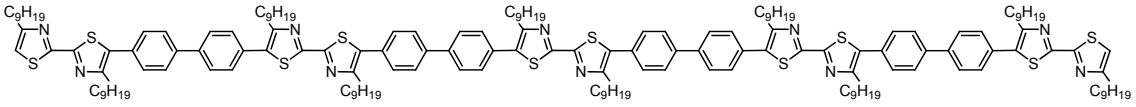
Calculated mass for H-($C_{36}H_{46}N_2S_2$)$_4$-Br : **2362.17047**

Peak 2, Found m/z : **2594.0427**



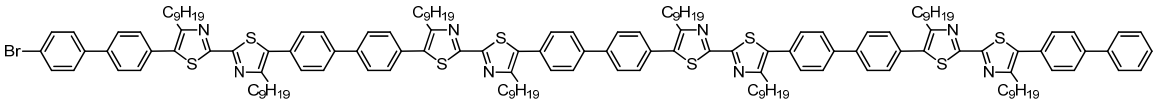
Calculated mass for Br-($C_{12}H_8$)-($C_{36}H_{46}N_2S_2$)$_4$-Br : **2594.14153**

Peak 3, Found m/z : **2702.6694**



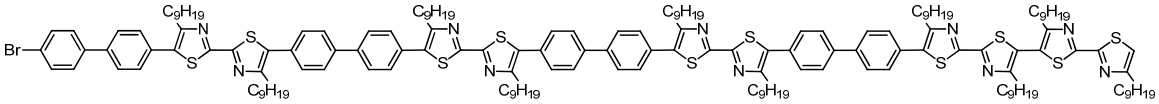
Calculated mass for H-($C_{36}H_{46}N_2S_2$)$_4$-($C_{24}H_{38}N_2S_2$)-H : **2702.50760**

Peak 4, Found m/z : **2515.3784**



Calculated mass for Br-($C_{12}H_8$)-($C_{46}H_{74}N_2S_2$)$_4$-H : **2514.23307**

Peak 5, Found m/z : **2781.4836**



Calculated mass for Br-($C_{12}H_8$)-($C_{46}H_{74}N_2S_2$)$_3$-($C_{24}H_{38}N_2S_2$)$_2$-H : **2780.41811**

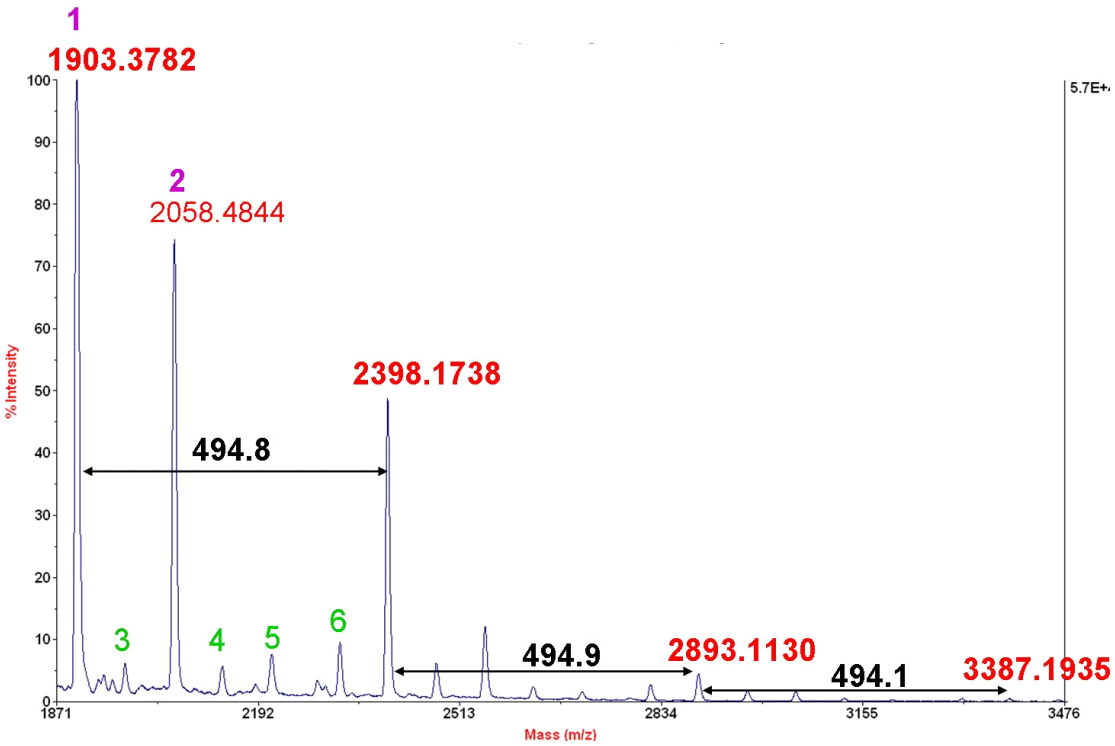
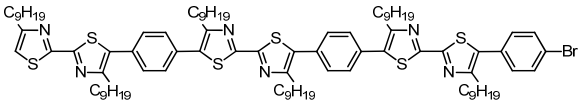


Figure S-14. Positive ion MALDI-TOF-MASS spectrum of **Polymer 3** (Table 2, Entry 4) using dithranol as a matrix and des-Arg^1-Bradykinin, Anglotensin I and Glu^1-Flibrinopeptide B as external standards.

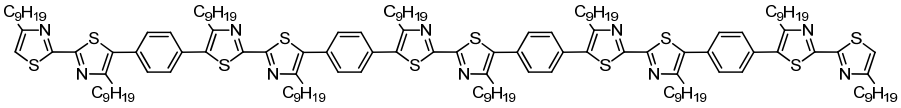
Calculated mass for the repeating unit: **494**

Peak 1, Found m/z : **1903.3782**



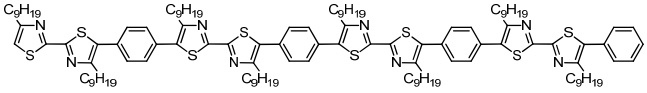
Calculated mass for H-($C_{30}H_{42}N_2S_2$)$_3$-Br : **1904.10346**

Peak 2, Found m/z : **2398.1738**



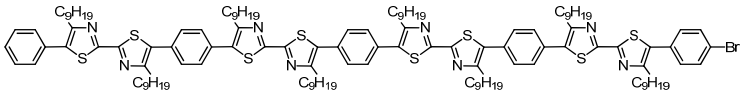
Calculated mass for H-$(C_{30}H_{42}N_2S_2)_4$-$(C_{24}H_{38}N_2S_2)$-H : **2398.39239**

Peak 3, Found m/z : **1980.1414**



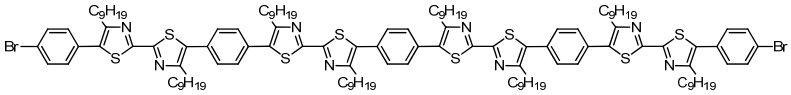
Calculated mass for H-$(C_{30}H_{42}N_2S_2)_4$-H : **1980.13476**

Peak 4, Found m/z : **2134.6445**



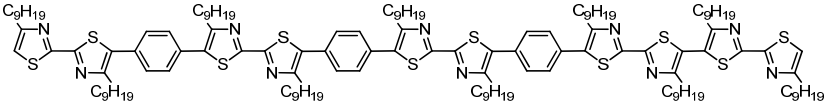
Calculated mass for C_6H_5-$(C_{30}H_{42}N_2S_2)_4$-Br : **2134.07657**

Peak 5, Found m/z : **2213.4717**



Calculated mass for Br-(C_6H_4)-$(C_{30}H_{42}N_2S_2)_4$-Br : **2213.89503**

Peak 6, Found m/z : **2322.2290**



Calculated mass for H-$(C_{30}H_{42}N_2S_2)_3$-$(C_{24}H_{38}N_2S_2)_2$-H : **2322.35109**

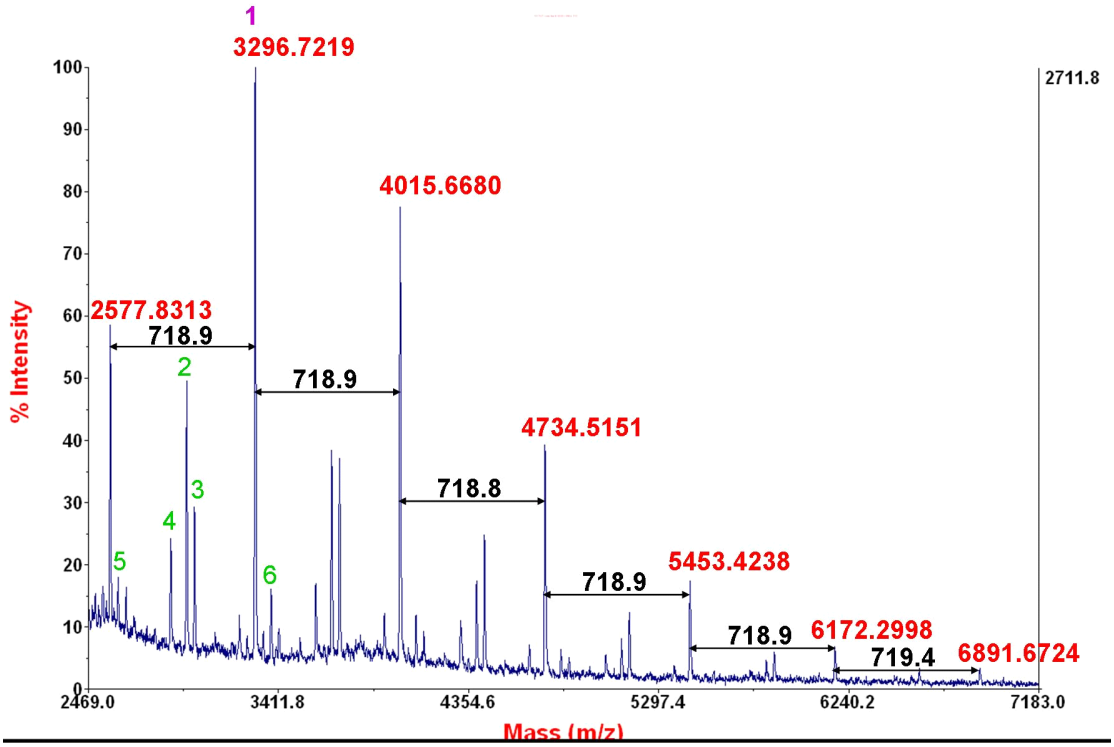
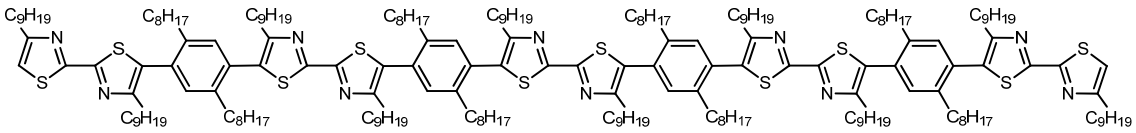


Figure S-15. Positive ion MALDI-TOF-MASS spectrum of **Polymer 4** (Table 2, Entry 6) using dithranol as a matrix and des-Arg^1-Bradykinin, Anglotensin I and Glu^1-Flibrinopeptide B as external standards.

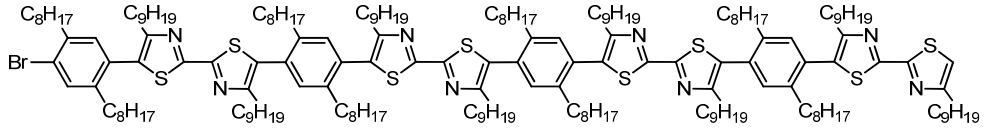
Calculated mass for the repeating unit: **718**

Peak 1, Found m/z : **3296.7219**



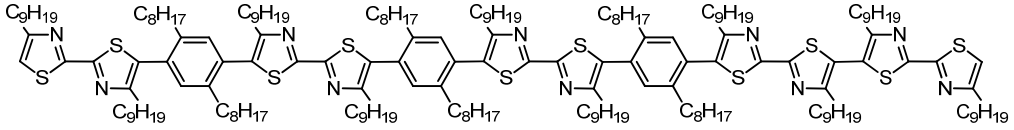
Calculated mass for H-($C_{46}H_{74}N_2S_2$)$_4$-($C_{24}H_{38}N_2S_2$)-H : **3296.38737**

Peak 2, Found m/z : **2957.0093**



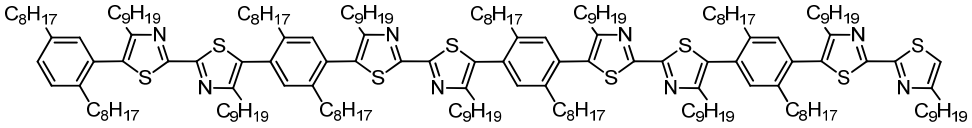
Calculated mass for Br-($C_{46}H_{74}N_2S_2$)$_4$-H : **2956.05022**

Peak 3, Found m/z : **2996.3965**



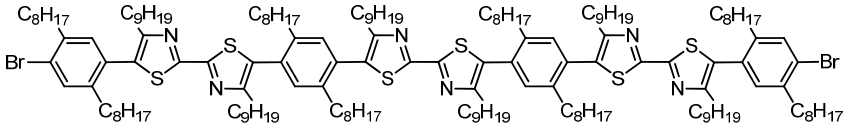
Calculated mass for H-($C_{46}H_{74}N_2S_2$)$_3$-($C_{24}H_{38}N_2S_2$)$_2$-H : **2996.10565**

Peak 4, Found m/z : **2878.1643**



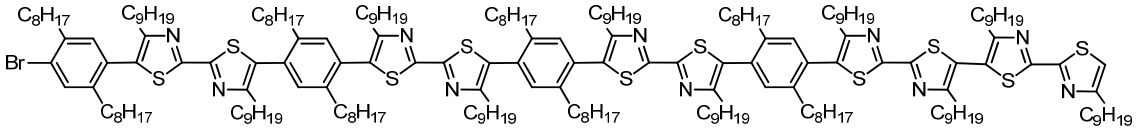
Calculated mass for H-$(C_{46}H_{74}N_2S_2)_4$-H : **2878.13971**

Peak 5, Found m/z : **2616.7969**



Calculated mass for Br-$(C_{22}H_{36})$-$(C_{46}H_{74}N_2S_2)_3$-Br : **2616.70769**

Peak 6, Found m/z : **3375.6929**



Calculated mass for Br-$(C_{22}H_{36})$-$(C_{46}H_{74}N_2S_2)_3$-$(C_{24}H_{38}N_2S_2)_2$-H : **3374.29786**

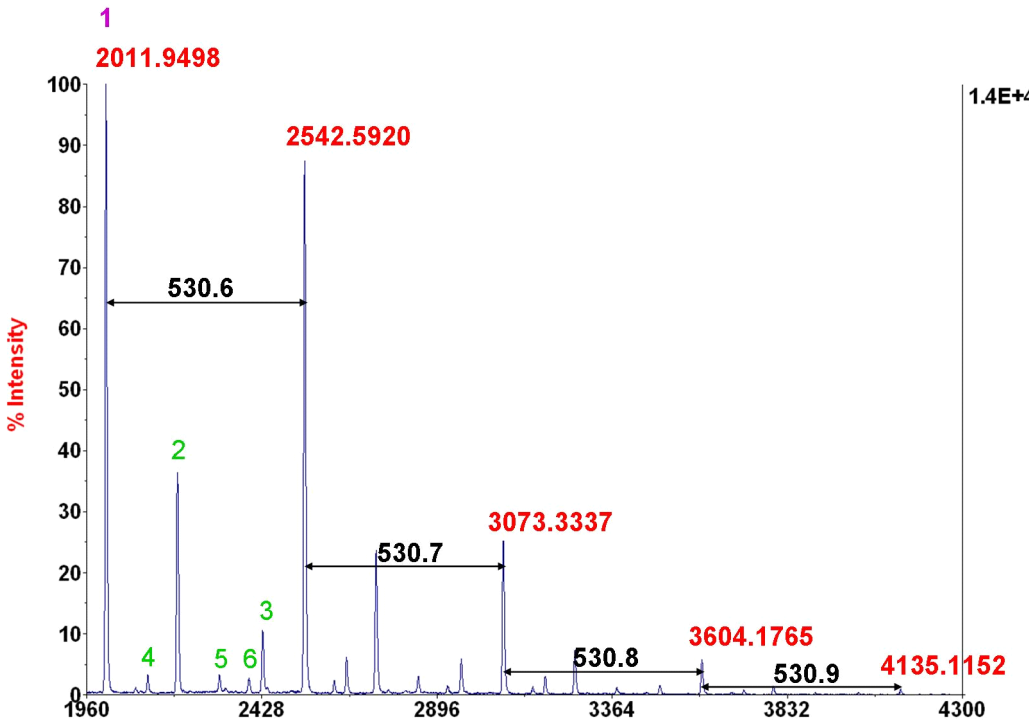
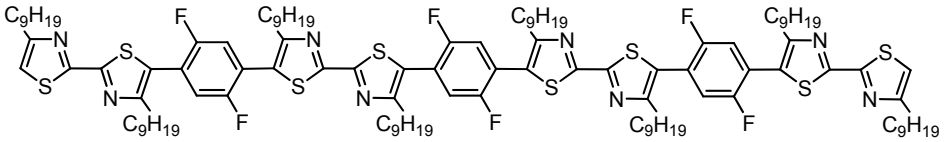


Figure S-16. Positive ion MALDI-TOF-MASS spectrum of **Polymer 5** (Table 2, Entry 7) using dithranol as a matrix and des-Arg[1]-Bradykinin, Anglotensin I and Glu[1]-Flibrinopeptide B as external standards.

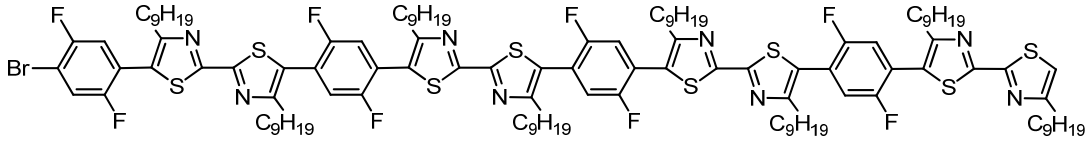
Calculated mass for the repeating unit: **530**

Peak 1, Found m/z : **2011.9498**



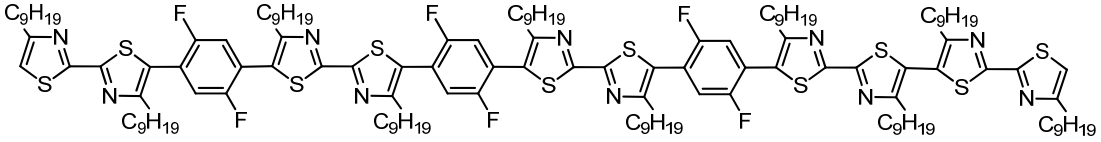
Calculated mass for H-($C_{30}H_{40}F_2N_2S_2$)$_3$-($C_{24}H_{38}N_2S_2$)-H : **2012.04692**

Peak 2, Found m/z : **2202.9626**



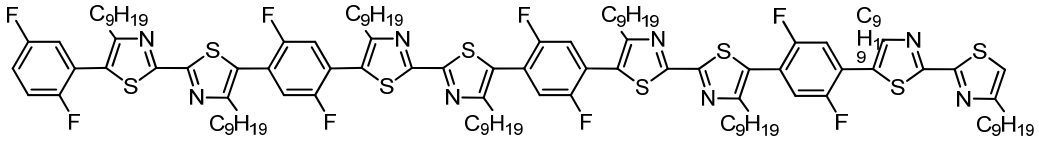
Calculated mass for Br-($C_{30}H_{40}F_2N_2S_2$)$_4$-H : **2201.96989**

Peak 3, Found m/z : **2430.6316**



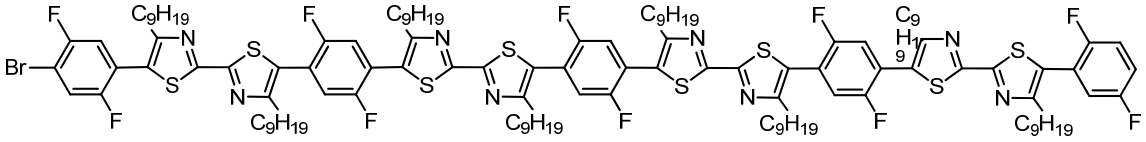
Calculated mass for H-($C_{30}H_{40}F_2N_2S_2$)$_3$-($C_{24}H_{38}N_2S_2$)$_2$-H : **2430.29456**

Peak 4, Found m/z : **2123.9712**



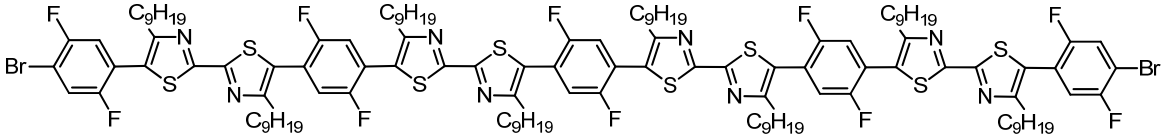
Calculated mass for H-$(C_{30}H_{40}F_2N_2S_2)_4$-H : **2124.05938**

Peak 5, Found m/z : **2315.1282**



Calculated mass for Br-$(C_6H_2F_2)$-$(C_{30}H_{40}F_2N_2S_2)_4$-H : **2313.98235**

Peak 6, Found m/z : **2393.9773**



Calculated mass for Br-$(C_6H_2F_2)$-$(C_{30}H_{40}F_2N_2S_2)_4$-Br : **2393.89081**

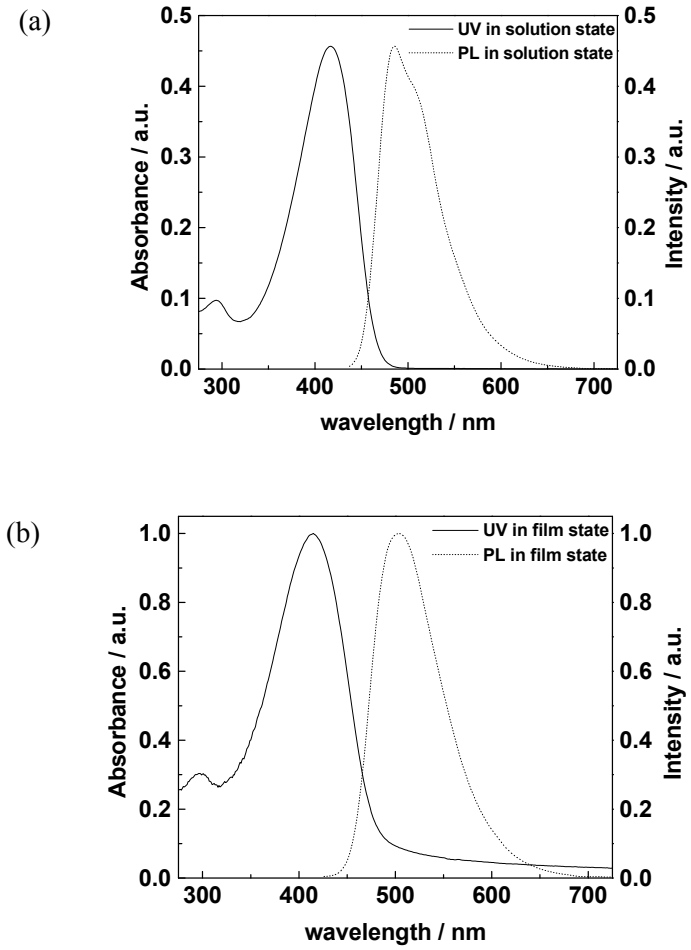
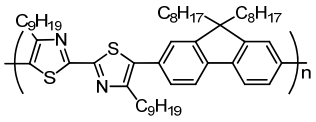
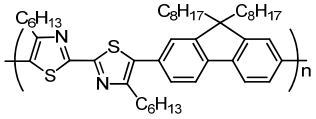


Figure S-17. UV-vis absorption and photoluminescence spectra of **Polymer 1** (Table 1, Entry 4) (a) in the solution state (1×10^{-5} M in $CHCl_3$) and (b) in the film state.

Table S-1. Photophysical properties of **Polymer 1** and the reference polymer [S1]

	Solution		Film	
	$\lambda_{max,\ abs}$ (nm)	$\lambda_{max,\ em}$ (nm)	$\lambda_{max,\ abs}$ (nm)	$\lambda_{max,\ em}$ (nm)
 **Polymer 1**	417	485	415	504
 Synthesized by the Suzuki−Miyaura cross-coupling reaction	412	489	413	513

[S1] J. Lee, B.-J. Jung, S. K. Lee, J.-I. Lee, H.-J. Cho and H.-K. Shim, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 1845.