Electronic Supplementary Information

Room Temperature Synthesis of Polythioamides from Multicomponent Polymerization of Sulfur, Pyridine-activated Alkyne, and Amines

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Materials and instruments

Alkyne **2a** was synthesized according to the literatures.[1,2] 2,6-Dibromopyridine, 1,3-diethynylbenzene **2b** and diamines **3a-d** were purchased from TCI; sublimed sulfur **1**, Na_2CO_3, K_2CO_3, Mg_2SO_4, $HgCl_2$, $ZnCl_2$, and HCl (36-38 wt%) were purchased from Guangzhou Chemical Reagent Factory; $CuCl_2$ and $FeCl_3$ were purchased from Energy Chemical; $NiCl_2 \cdot 6H_2O$ was purchased from Alfa-Aesar; $CdCl_2$ was purchased from Aladdin; dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), pyridine, *i*-Pr_2NH, trimethylsilylacetylene and CuI were purchased from Energy Chemical; $Pd(PPh_3)_2Cl_2$ was purchased from Boka; tetrahydrofuran (THF), dichloromethane (DCM), methanol (MeOH) and ethyl acetate (EA) were purchased from Guangzhou Chemical Reagent Factory. All reactants and reagents were used without further purification.

^1H and ^{13}C NMR spectra were estimated on a Brucker Avance 400 or 500 MHz NMR spectrometer using deuterated dimethyl sulfoxide (DMSO-d_6) as solvent and tetramethylsilane (TMS, $\delta = 0$) as internal reference. FT-IR spectra were determined on a Bruker Vector 33 FT-IR spectrometer. High resolution mass spectra measurements were carried out on a Bruker maxis impact mass spectrometer. The number-(M_n) and weight-(M_w) average molecular weights and polydispersity indices (PDI = M_w/M_n) of the polymers were estimated by a Waters 1515 gel permeation chromatography system. DMF/LiBr solution (0.05 M of LiBr) was used as eluent at a flow rate of 1 mL/min. A set of monodispersed polystyrenes, covering the M_w range of 10^3-10^7 g/mol, were utilized as standards for molecular weight calibration. Single crystal X-ray diffraction patterns were measured by an X'pert Pro Panalytical X-ray diffractometer at an incident angle ranging from 5 to 50°. X-ray photoelectron spectroscopy was performed using a Kratos Axis Ultra DLD spectrometer with a monochromated Al Kα X-ray source at a residual pressure of 5×10^{-9} torr. The concentrations of metal ions were measured by Z-2000 atomic absorption spectrophotometer (AAS). The concentrations of mercury ion were measured by an AFS-9130 atomic fluorescence spectrometer. UV-vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. Fluorescence spectra were recorded on a Horiba Fluoromax-4 fluorescence spectrophotometer. The hand-held UV lamp (GD-13) used for photo-induced emission enhancement was purchased from Shengjiameixin, and the wavelength and power of the LED UV lamp is 365 nm and 20 W, respectively.

Synthetic procedures and characterization data

2,2'-(Pyridine-2,6-diyl)bis(*N*-benzylethanethioamide) 4: Into a 10 mL Schlenk tube equipped with a magnetic stir bar were added elemental sulfur (**1**, 320.0 mg, 10 mmol) and 2,6-diethynylpyridine (**2a**, 508.6 mg, 4 mmol) under nitrogen atmosphere. Phenyl methanamine (**6**, 1.09 mL, 10 mmol) and 3 mL of pyridine were then injected into the tube by syringe. After stirring at 80 °C for 24 h, 20 mL of water was added and the reaction mixture was extracted with dichloromethane for three times (3 × 50 mL). The organic phases were combined and the solvent was removed under reduced pressure to afford the crude product, which was then purified by column chromatography on silica gel using dichloromethane/ethyl acetate mixture (100/1 v/v) as eluent. A light yellow solid was obtained in 45% yield. ^{1}H NMR (400 MHz, DMSO-d_6), δ (TMS, ppm): 10.75 (s, 2H, HN-C=S), 7.72 (s, 1H), 7.33-7.26 (m, 12H), 4.81 (s, 4H), 4.16 (s, 4H). ^{13}C NMR (125 MHz, DMSO-d_6), δ (TMS, ppm): 199.48 (C=S), 156.17, 137.13, 136.92, 128.24, 127.55, 127.04, 121.43, 53.00, 48.41. IR (KBr disk), υ (cm^{-1}): 3343, 3160, 1548, 1524, 1495, 1453, 1417, 1344, 1126, 751, 696.

2,2'-(1,3-Phenylene)bis(*N*-benzylethanethioamide) 5: Elemental sulfur (**1**, 1.28 g, 40 mmol) was added into a 50 mL Schlenk tube equipped with a magnetic stir bar. 15 mL of pyridine, 1,3-diethynylbenzene (**2b**, 2.12 ml, 16 mmol) and phenyl methanamine (**6**, 4.37 mL, 40 mmol) were then injected into the tube by syringe. After stirring at 80 °C for 24 h, 30 mL of water was added and the reaction mixture was extracted with dichloromethane for three times (3 × 50 mL). The organic phases were combined and the solvent was removed under reduced pressure to afford the crude product, which was purified by column chromatography on silica gel using petroleum ether/ethyl acetate mixture (5/1 v/v) as eluent. A yellow solid was obtained in 58% yield. ^{1}H NMR (400 MHz, DMSO-d_6), δ (TMS, ppm): 10.64 (s, 2H, HN-C=S), 7.35-7.32 (m, 5H), 7.30-7.25 (m, 6H), 7.23 (s, 3H), 4.78 (s, 4H), 3.94 (s, 4H). ^{13}C NMR (125 MHz, DMSO-d_6), δ (TMS, ppm): 201.91 (C=S), 137.87, 137.55, 129.84, 128.88, 128.50, 128.25, 127.70, 127.55, 51.69, 49.15. IR (KBr disk), υ (cm^{-1}): 3350, 3200, 3031, 2915, 1524, 1450, 1399, 1344, 1128, 966, 744, 693.

General procedure of the multicomponent polymerization of activated alkynes, elemental sulfur, and aliphatic diamines. The synthesis of P**1** was given below as an example. Into a 10 mL Schlenk tube equipped with a magnetic stir bar were added elemental sulfur (**1**, 76.9 mg, 2.4 mmol), 2,6-diethynylpyridine (**2a**, 114.4 mg, 0.9 mmol), and 1,4-phenylenedimethanamine (**3a**, 81.7 mg, 0.6 mmol) under nitrogen. 2 mL of pyridine was then injected by a syringe to dissolve the monomers and the polymerization solution was stirred at 40 ºC for 4 h. Afterwards, the polymerization mixture was precipitated by dropping into 100 mL of methanol through a cotton filter. The precipitate was filtered and washed with methanol (3 × 30 mL), which was then dried under vacuum at 40 °C to a constant weight.

P**1** was obtained as a yellow solid in 98% yield. M_w = 95 100 g/mol, $M_\mathrm{w}/M_\mathrm{n}$ = 3.43. ^{1}H NMR (400 MHz, DMSO-d_6), δ (TMS, ppm): 10.73 (2H, HN-C=S), 7.69 (1H), 7.31–7.25 (m, 6H), 4.77 (4H), 4.14 (4H). ^{13}C NMR (125 MHz, DMSO-d_6), δ (TMS, ppm): 199.44 (C=S), 156.10, 137.16, 135.85, 127.62, 121.43, 52.99, 48.18. IR (KBr disk), υ (cm^{-1}): 3347, 3214, 1524, 1448, 1402, 1337, 1112, 808, 750.

P**3** was obtained as a yellowish brown solid in 98% yield. M_w = 36 200 g/mol, $M_\mathrm{w}/M_\mathrm{n}$ = 1.54. ^{1}H NMR (500 MHz, DMSO-d_6), δ (TMS, ppm): 10.32 (2H, HN-C=S), 7.68 (1H), 7.19 (2H), 4.06 (4H), 3.52 (4H), 1.58 (4H), 1.31 (4H). ^{13}C NMR (125 MHz, DMSO-d_6), δ (TMS, ppm): 199.09 (C=S), 156.75, 137.68, 121.78, 53.60, 45.81, 27.56, 26.68. IR (KBr disk), υ (cm^{-1}): 3480, 3211, 2926, 1535, 1450, 1405, 1078, 810, 743, 623.

P**4** was obtained as a yellowish brown solid in 82% yield. M_w = 16 400 g/mol, $M_\mathrm{w}/M_\mathrm{n}$ = 1.19. ^{1}H NMR (400 MHz, DMSO-d_6), δ (TMS, ppm): 10.11 (2H, HN-C=S), 7.64 (2H), 7.21 (2H), 4.13 (4H), 3.58 (4H), 0.94 (6H). ^{13}C NMR (125 MHz, DMSO-d_6), δ(TMS, ppm): 200.64 (C=S), 156.73, 150.08, 137.74, 136.61, 124.38, 121.83, 67.49, 54.11, 53.07, 49.73, 40.91, 25.60, 24.17. IR (KBr disk), υ (cm^{-1}): 3442, 3205, 2963, 1660, 1581, 1523, 1448, 1410.

P**5** was obtained as an orange solid in 95% yield. M_w = 11 600 g/mol, $M_\mathrm{w}/M_\mathrm{n}$ = 1.10. ^{1}H NMR (400 MHz, DMSO-d_6), δ (TMS, ppm): 7.73 (1H), 7.28 (2H), 5.33 (2H), 4.36 (4H), 3.17 (4H), 3.03 (2H), 1.72 (2H), 1.55 (4H), 1.23-1.12 (8H), 0.81 (2H). ^{13}C NMR (125 MHz, DMSO-d_6), δ(TMS, ppm): 195.90 (C=S), 156.62, 137.88, 121.40, 67.49, 52.78, 51.12, 50.43, 43.84, 36.01, 34.91, 33.27, 31.83, 28.98, 25.60, 23.34. IR (KBr disk), υ (cm^{-1}): 3439, 2923, 2847, 1627, 1581, 1555, 1499, 1450, 1274.

Synthetic procedure of P2. Elemental sulfur (**1**, 128.2 mg, 4.0 mmol), 1,3-diethynylbenzene (**2b**, 189.2 mg, 1.5 mmol), and 1,4-phenylenedimethanamine (**3a**, 136.2 mg, 1.0 mmol) were added into a 10 mL Schlenk tube equipped with a magnetic stir bar under nitrogen. 1.5 mL of pyridine was then injected by a syringe to dissolve the monomers and stirred at 90 °C for 4 h. Afterwards, the polymerization mixture was precipitated by dropping it into 100 mL of methanol through a cotton filter. P**2** was obtained as a yellow solid in 84% yield. M_w = 59 100 g/mol, M_w/M_n = 2.11. ^{1}H NMR (400 MHz, DMSO-d_6), δ(TMS, ppm): 10.63 (s, 2H, HN-C=S), 7.46 (s, 1H), 7.35 (s, 2H), 7.25–7.22 (m, 5H), 4.75 (s, 4H), 3.93 (s, 4H). ^{13}C NMR (125 MHz, DMSO-d_6), δ (TMS, ppm): 201.88 (C=S), 201.44 (C=S), 138.49, 137.84, 136.55, 132.57, 130.44, 129.95, 129.07, 128.52, 128.32, 127.52, 122.00, 83.92, 81.16, 51.71, 51.16, 48.85. IR (KBr disk), υ (cm^{-1}): 3346, 3215, 1520, 1399, 1335, 1122.

Procedures for metal ions extraction

(a) Selectivity test with different metal ions. Into 10 mL aqueous solutions of NaCl, KCl, $MgCl_2$, $FeCl_3$, $CuCl_2$, $ZnCl_2$, $NiCl_2 \cdot 6H_2O$, $CdCl_2$, and $HgCl_2$ ($[M^{n+}]_0$ = 100 mg/L) were added 100 μL DMF solution of P**1** (10 mg/mL)**,** respectively. After the mixtures were stirred at room temperature for 1 h, the remaining concentration of metal ions in the supernatant after centrifugation was then measured by Z-2000 atomic absorption spectrophotometer and AFS-9130 atomic fluorescence spectrometer to calculate the extraction efficiency.

(b) The procedure of mercury removal. Into 2 mL of $HgCl_2$ solution (60 mg/L) was added 0.1, 0.2, 0.4, 0.6 and 1.2 mg of P**1**, P**2**, and P**5** (10 mg/mL in DMF), respectively. After the mixtures were stirred at room temperature for 1 h, the remaining concentration of metal ions in the supernatant after centrifugation was then measured by AFS-9130 atomic fluorescence spectrometer to calculate the removal efficiency.

Table S1. Effect of temperature on the MCP of **1**, **2a**, and **3a**[a]

entry	T (°C)	yield (%)	M_w[b]	M_w/M_n[b]	*solubility*
1	25	98	35 400	1.57	√
2	30	97	49 200	1.96	√
3	40	98	95 100	3.43	√
4	50	97	87 700	3.35	Δ
5	60	96	95 500	3.32	Δ
6	70	96	75 600	2.67	Δ
7	80	97	55 500	2.05	Δ
8	90	98	48 200	1.82	Δ

[a] Carried out in pyridine for 4 h under nitrogen, [**3a**] = 0.3 M, 1/8[**S_8**]: [**2a**]: [**3a**] = 8.0: 3.0: 2.0. [b] M_w and M_n were determined by GPC in DMF based on polystyrene standard samples. √: the product is completely soluble, Δ: the product is partially soluble.

Table S2. Effect of solvent on the MCP of **1**, **2a**, and **3a**[a]

entry	solvent	yield (%)	M_w[b]	M_w/M_n[b]
1[c]	pyridine	98	95 100	3.43
2	DMF	97	60 100	2.12
3	DMSO	97	50 600	2.09
4	DMAc	90	28 700	1.42

[a] Carried out at 40 °C under nitrogen for 4 h, [**3a**] = 0.3 M, 1/8[**S_8**]: [**2a**]: [**3a**] = 8.0: 3.0: 2.0. [b] M_w and M_n were determined by GPC in DMF based on polystyrene standard samples. [c] Data was taken from Table S1, entry 3.

Table S3. Effect of monomer concentration on the MCP of **1**, **2a**, and **3a**[a]

entry	[**3a**] (M)	yield (%)	M_w[b]	M_w/M_n[b]
1	0.10	89	35 100	1.70
2[c]	0.30	98	95 100	3.43
3	0.50	87	33 000	1.60
4	1.00	gel		

[a]Carried out in pyridine at 40 °C under nitrogen for 4 h, 1/8[**S8**]: [**2a**]: [**3a**] = 8.0: 3.0: 2.0. [b]M_w and M_n were determined by GPC in DMF based on polystyrene standard samples. [c]Data was taken from Table S1, entry 3.

Table S4. Effect of monomer concentration on the MCP of **1**, **2b**, and **3a**[a]

entry	[**3a**] (M)	yield (%)	M_w[b]	M_w/M_n[b]
1	0.30	-		
2	0.50	31	19 100	1.33
3	0.67	84	59 100	2.11
4	1.00	98	28 200	1.43

[a]Carried out in pyridine at 90 °C under nitrogen for 4 h, 1/8[**S8**]: [**2b**]: [**3a**] = 8.0: 3.0: 2.0. [b] M_w and M_n were determined by GPC in DMF based on polystyrene standard samples.

Table S5. Crystal Data and Structure Refinement of Compounds **4** and **5**

Crystal	**4**	**5**
CCDC number	2121257	2121289
Empirical formula	$C_{23}H_{23}N_3S_2$	$C_{24}H_{24}N_2S_2$
Formula weight (g mol^{-1})	405.56	404.57
Temperature (K)	150(10)	150(10)
Wavelength (Å)	1.54184	1.54184
Absorption correction	multi-scan	multi-scan
Crystal system, space group	triclinic, P -1	monoclinic, P 2_1/c
Unit cell dimensions	a = 8.0848(2) Å	a = 10.0154(3) Å
	b = 8.7049(2) Å	b = 10.7382(2) Å
	c = 16.1850(4) Å	c = 38.8755(10) Å
	α = 75.398(2)	α = 90
	β = 78.016(2)	β = 95.253(3)
	γ = 68.556(3)	γ = 90
Volume (Å^3)	1017.50(5)	4163.40(18)
Z, Calculated density (g cm^{-3})	2, 1.324	8, 1.291
Absorption coefficient (mm^{-1})	2.465	2.394
F(000)	428	1712
Crystal size (mm^3)	0.07 × 0.07 × 0.08	0.08 × 0.10 × 0.15
Theta range for data collection (°)	2.845 to 67.080	4.273 to 72.355
Index ranges	-5 <= h <= 9	-8 <= h <= 12
	-10 <= k <= 10	-13 <= k <= 13
	-19 <= l <= 19	-47 <= l <= 47
Reflections collected	8651	10293
Independent reflections	3574 [R(int) = 0.0284]	10293 [R(int) = 0.1186]
completeness to theta	97.8 %, 66.968°	99.9 %, 67.684°
Max. and min. transmission	1.00000 and 0.83224	1.00000 and 0.71291
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3574 /1/253	10293/0/505
Goodness-of-fit on F^2	1.072	1.029
Final *R* indices [I > 2sigma(I)]	R1 = 0.0315, wR2 = 0.0813	R1 = 0.0799, wR2 = 0.2233
R indices (all data)	R1 = 0.0345, wR2 = 0.0830	R1 = 0.0868, wR2 = 0.2283
Largest diff. peak and hole	0.175 and -0.228 e.Å^{-3}	0.634 and -0.427 e.Å^{-3}

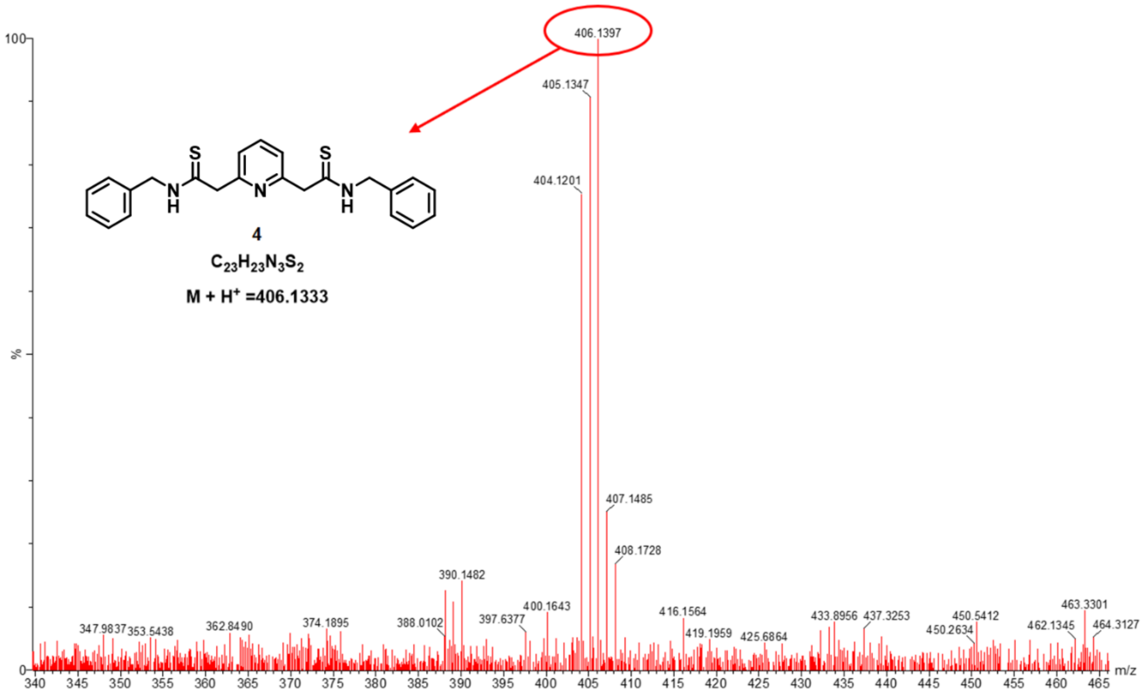

Fig. S1 HRMS spectrum of model compound **4**.

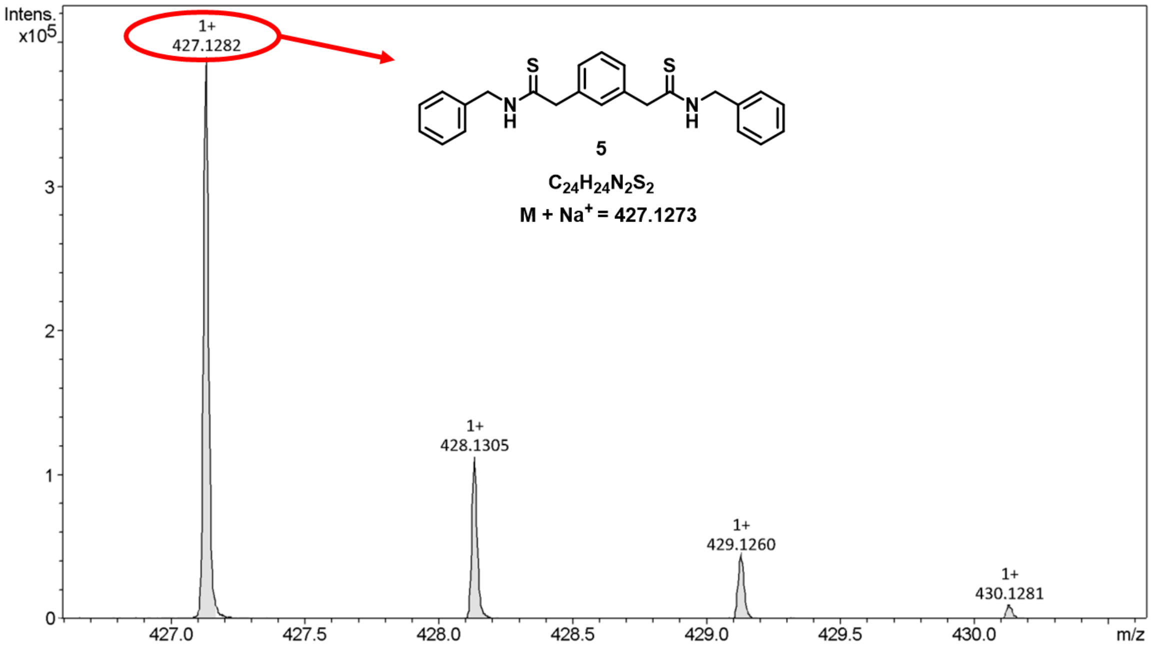

Fig. S2 HRMS spectrum of model compound **5**.

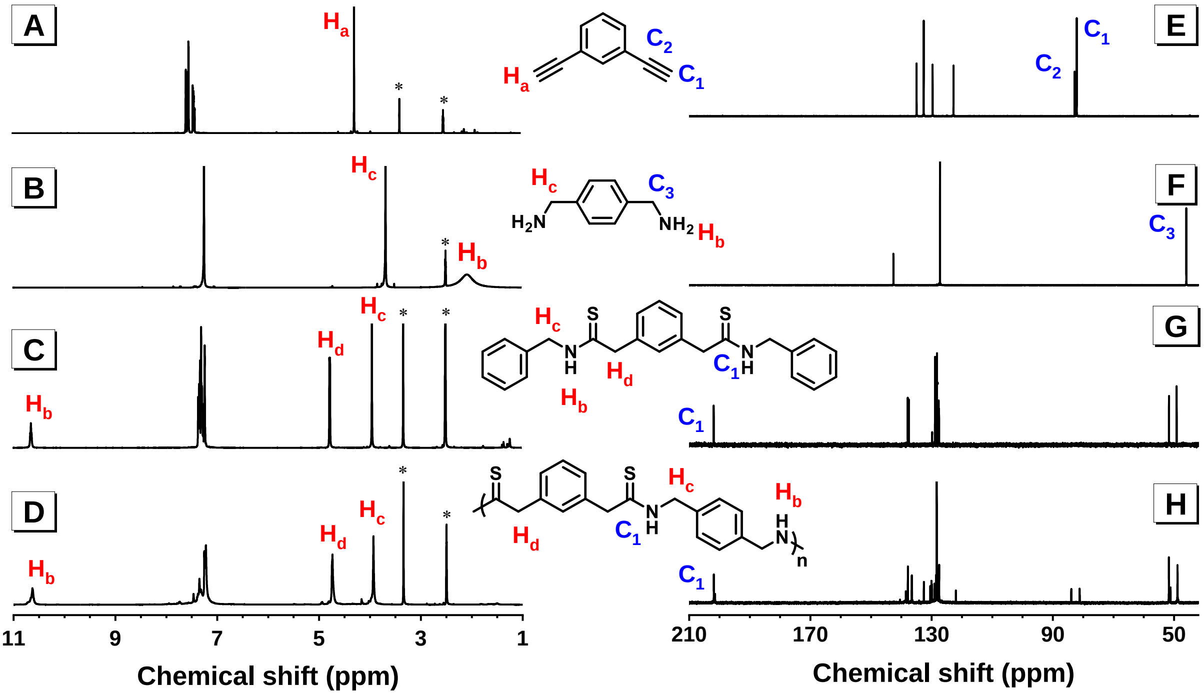

Fig. S3 ^{1}H NMR spectra of (A) **2b**, (B) **3a**, (C) **5**, and (D) P**2** in DMSO-*d*6. ^{13}C NMR spectra of (E) **2b**, (F) **3a**, (G) **5** and (H) P**2** in DMSO-*d*6. The solvent peaks were marked with asterisks.

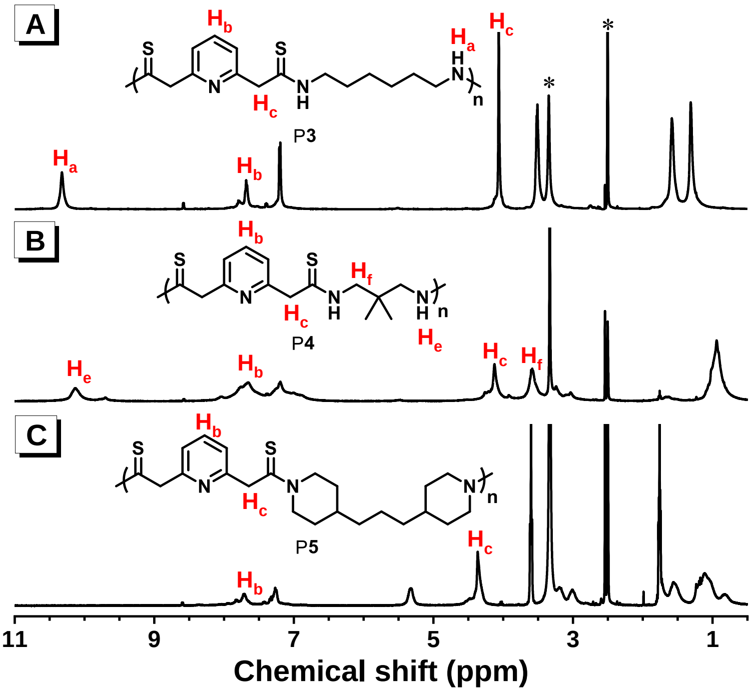

Fig. S4 ^{1}H NMR spectra of (A) P**3**, (B) P**4**, and (C) P**5** in DMSO-*d*6. The solvent peaks were marked with asterisks.

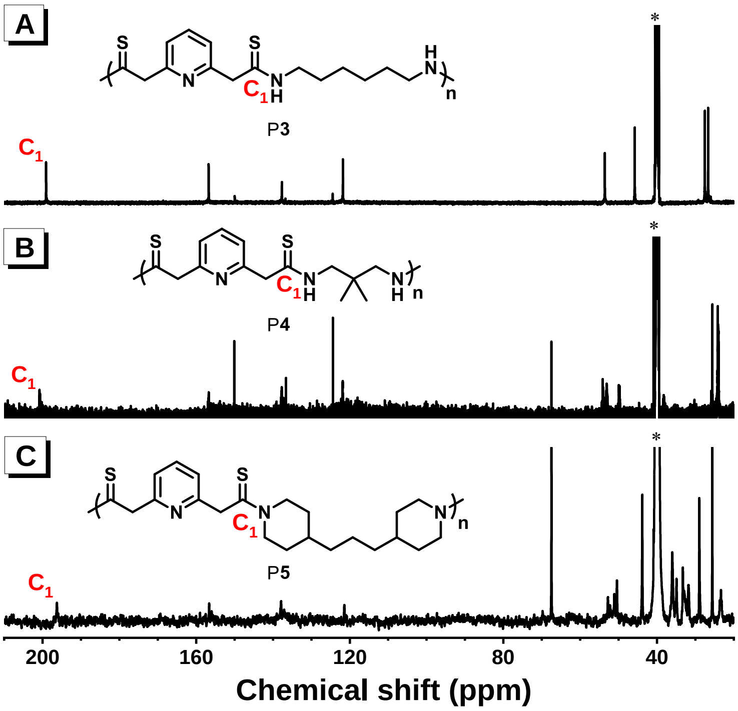

Fig. S5 ^{13}C NMR spectra of (A) P**3**, (B) P**4**, and (C) P**5** in DMSO-*d*6. The solvent peaks were marked with asterisks.

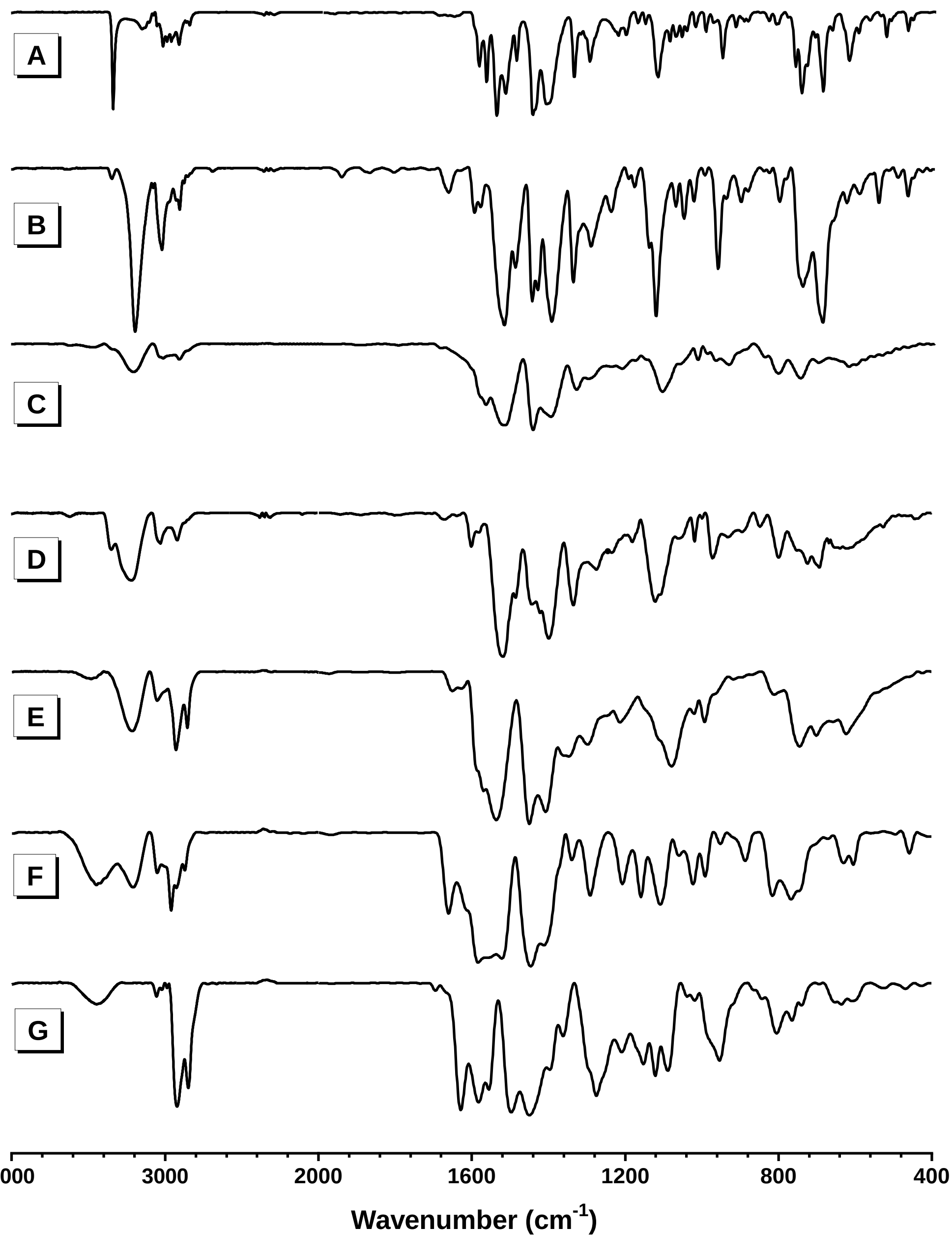

Fig. S6 FT-IR spectra of (A) **4**, (B) **5**, (C) P**1**, (D) P**2**, (E) P**3**, (F) P**4** and (G) P**5**.

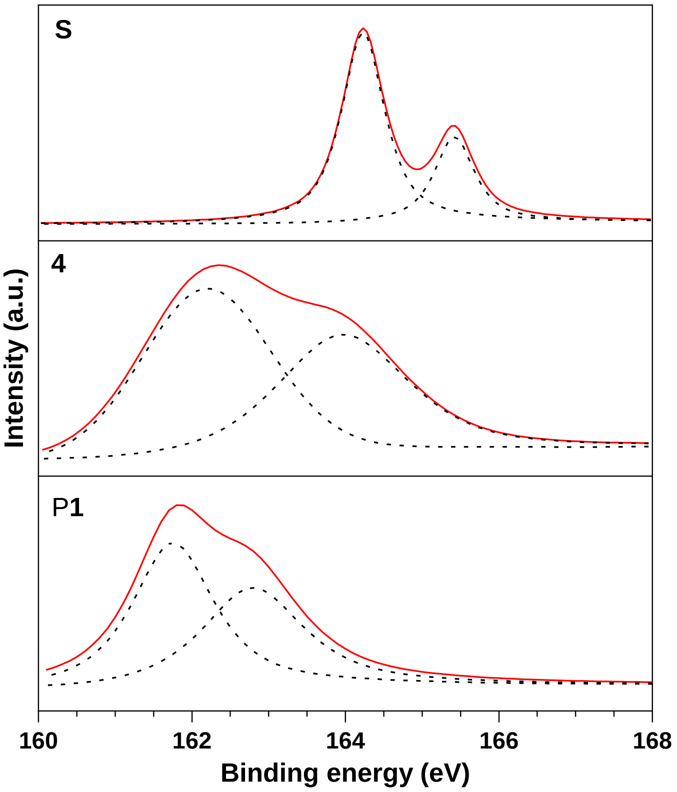

Fig. S7 S 2p XPS of elemental sulfur, model compound **4** and P**1**.

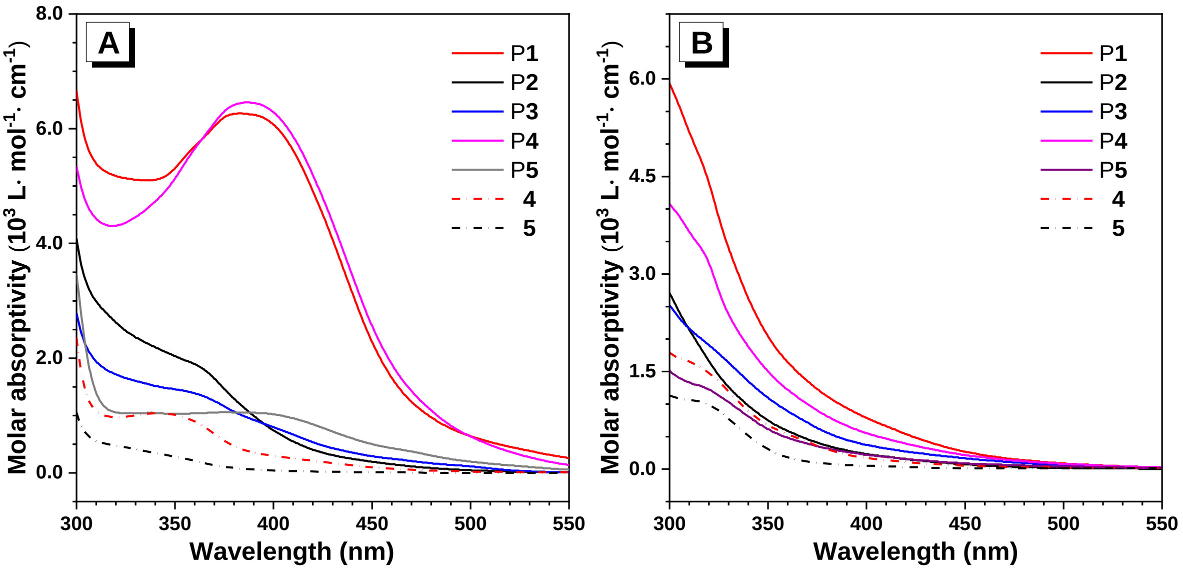

Fig. S8 Absorption spectra of the DMF solutions of polythioamides and model compounds (A) before and (B) after the illumination of 365 nm light with a hand-held UV lamp for 30 min. Concentration: 100 μM.

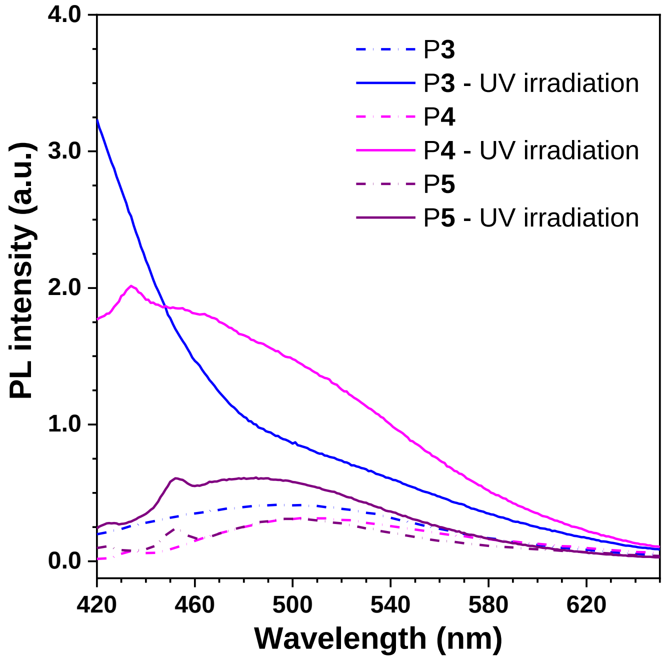

Fig. S9 PL spectra of the DMF solutions of P**3**, P**4** and P**5** before and after the illumination of 365 nm light with a hand-held UV lamp for 30 min. Concentration: 100 μM. Excitation wavelength: P**3** (359 nm), P**4** (386 nm), P**5** (400 nm).

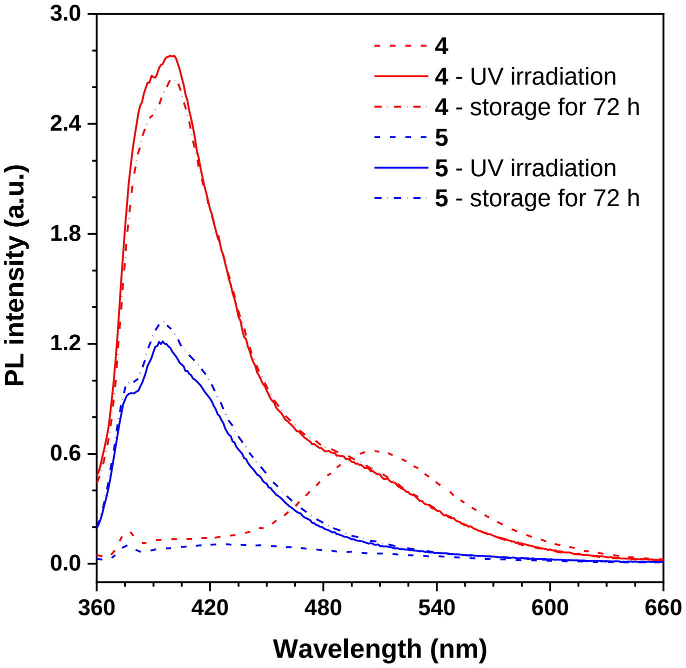

Fig. S10 PL spectra of DMF solutions of **4** and **5** before and after the illumination of 365 nm light with a hand-held UV lamp for 30 min, and further stored for 72 h in dark. Concentration: 100 μM. Excitation wavelength: 340 nm.

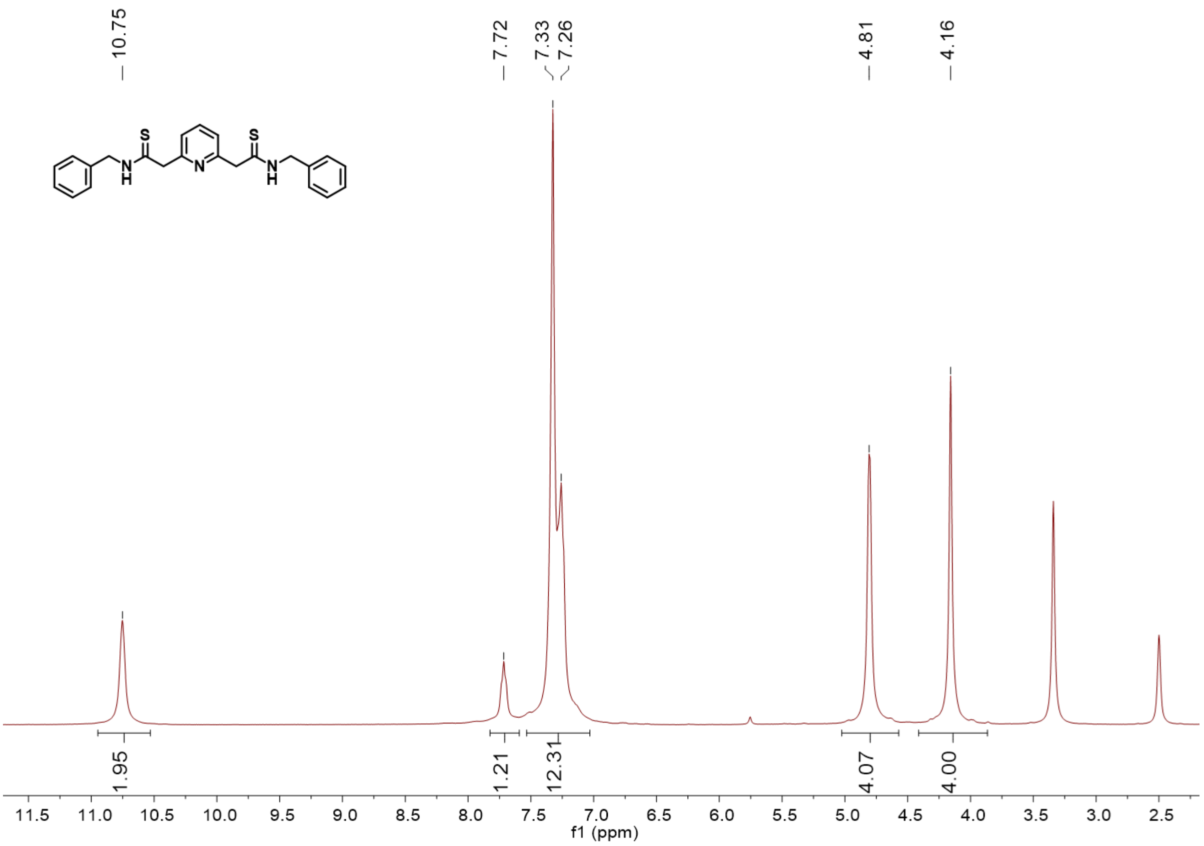

Fig. S11 ^{1}H NMR spectrum of **4** in DMSO-d_6.

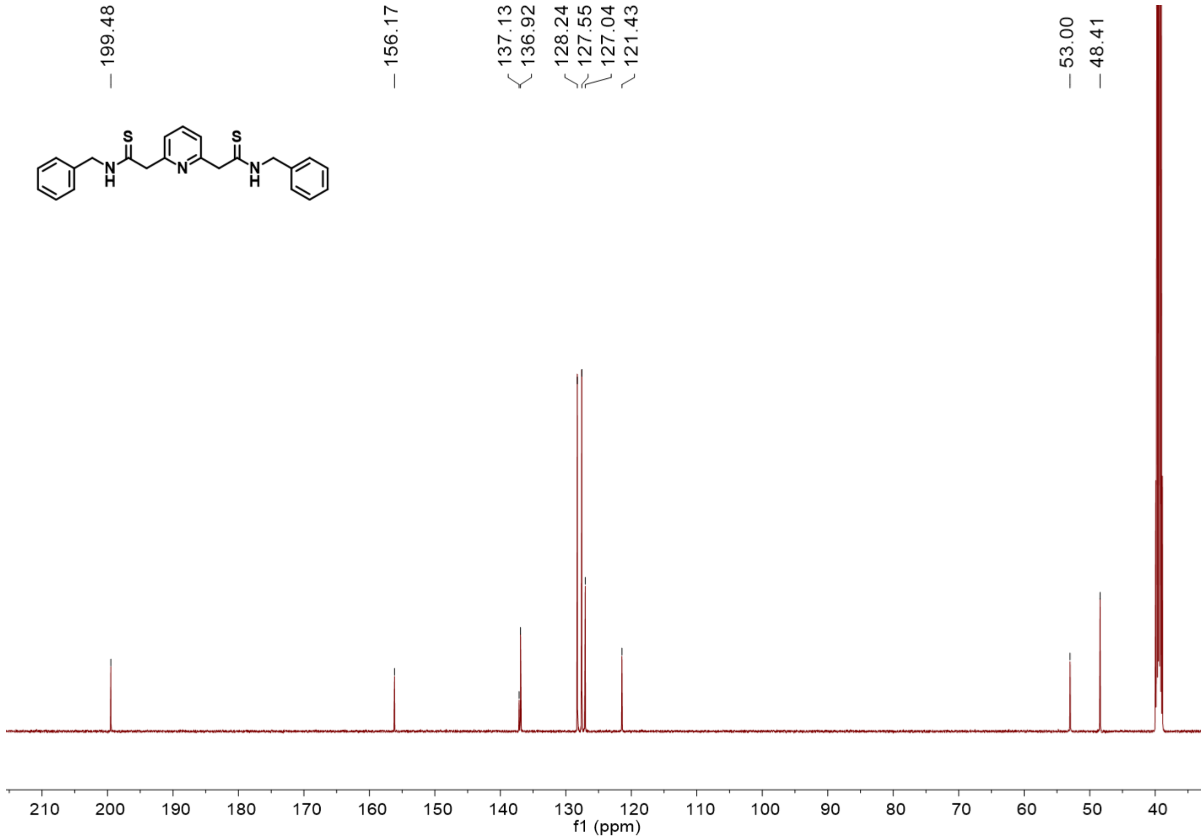

Fig. S12 ^{13}C NMR spectrum of **4** in DMSO-d_6.

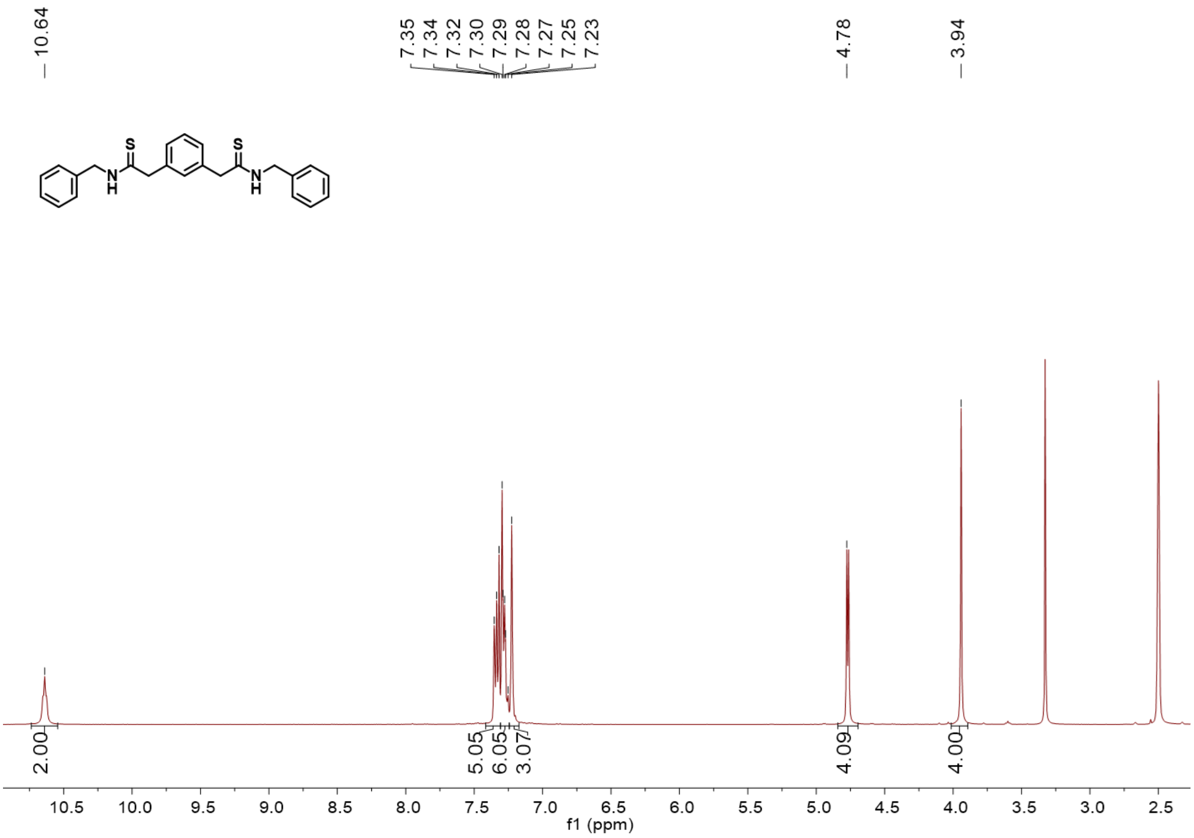

Fig. S13 ^{1}H NMR spectrum of **5** in DMSO-d_6.

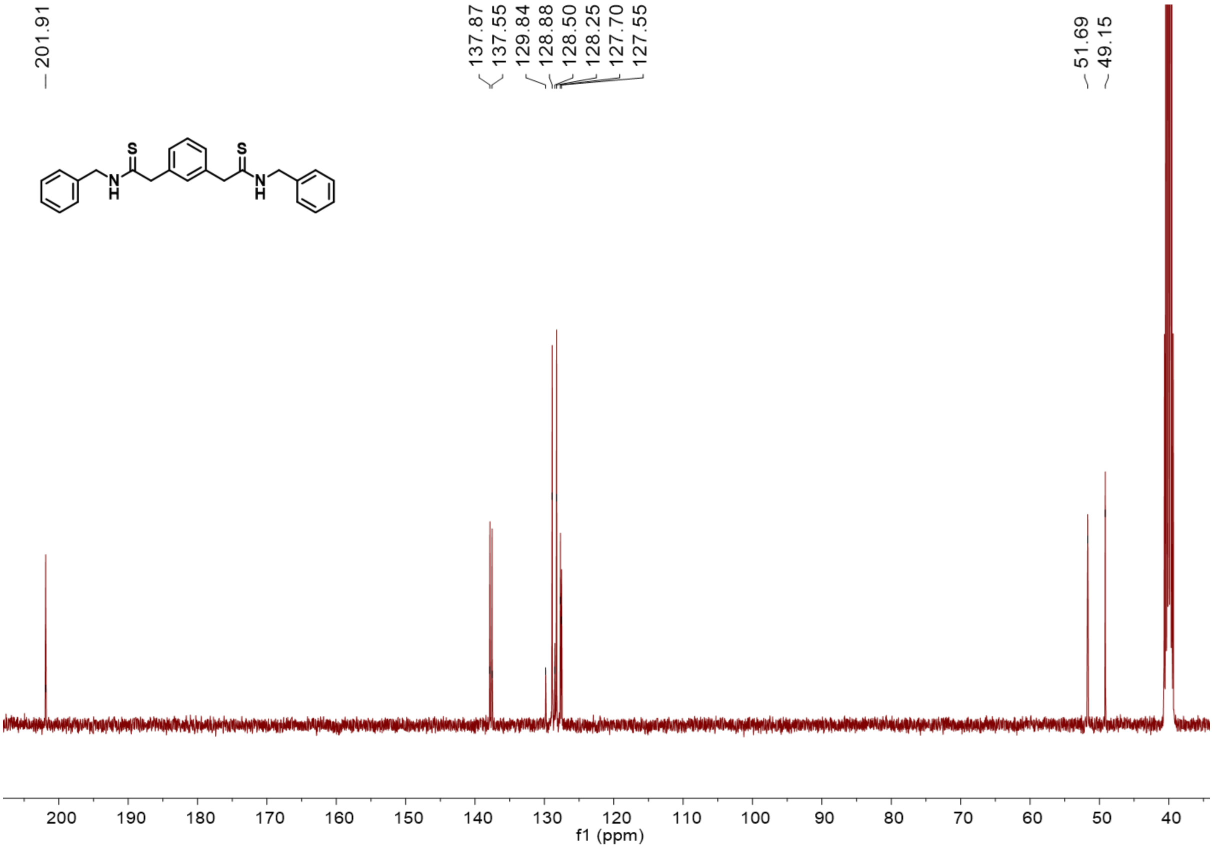

Fig. S14 ^{13}C NMR spectrum of **5** in DMSO-d_6.

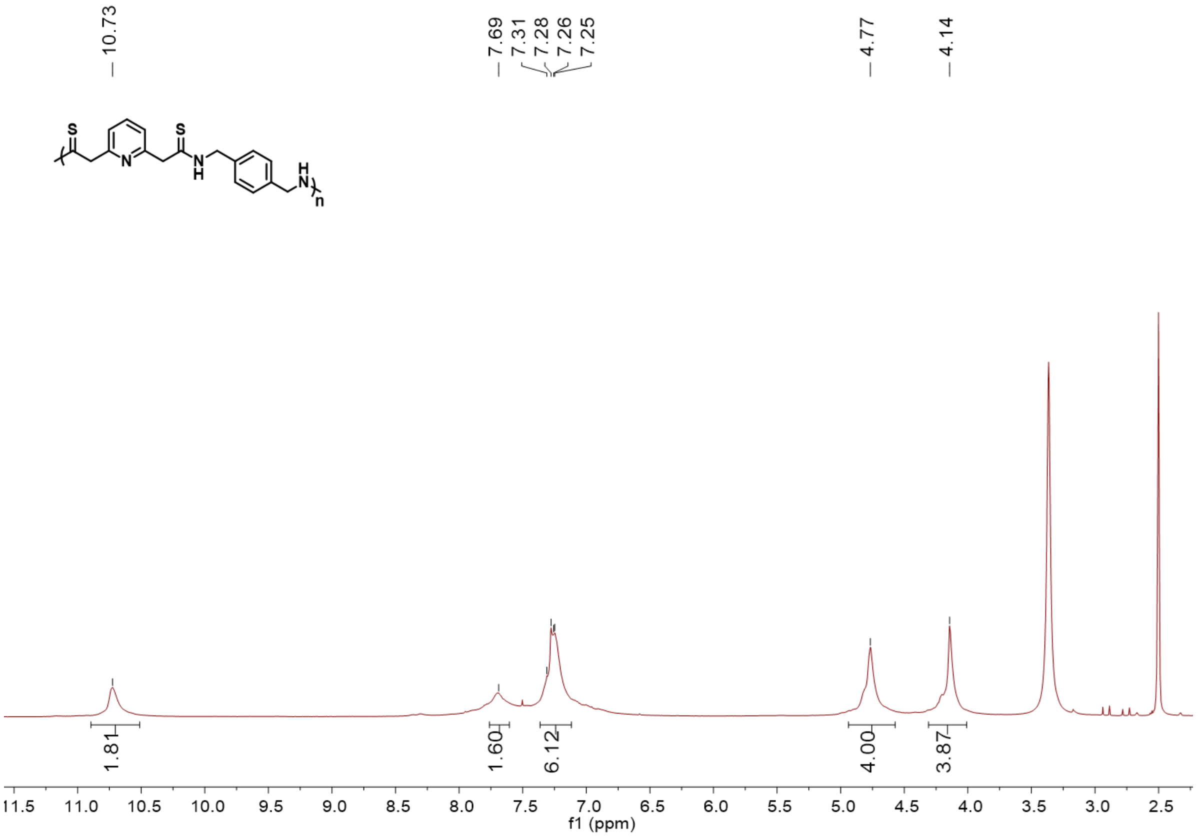

Fig. S15 ^{1}H NMR spectrum of P**1** in DMSO-d_6.

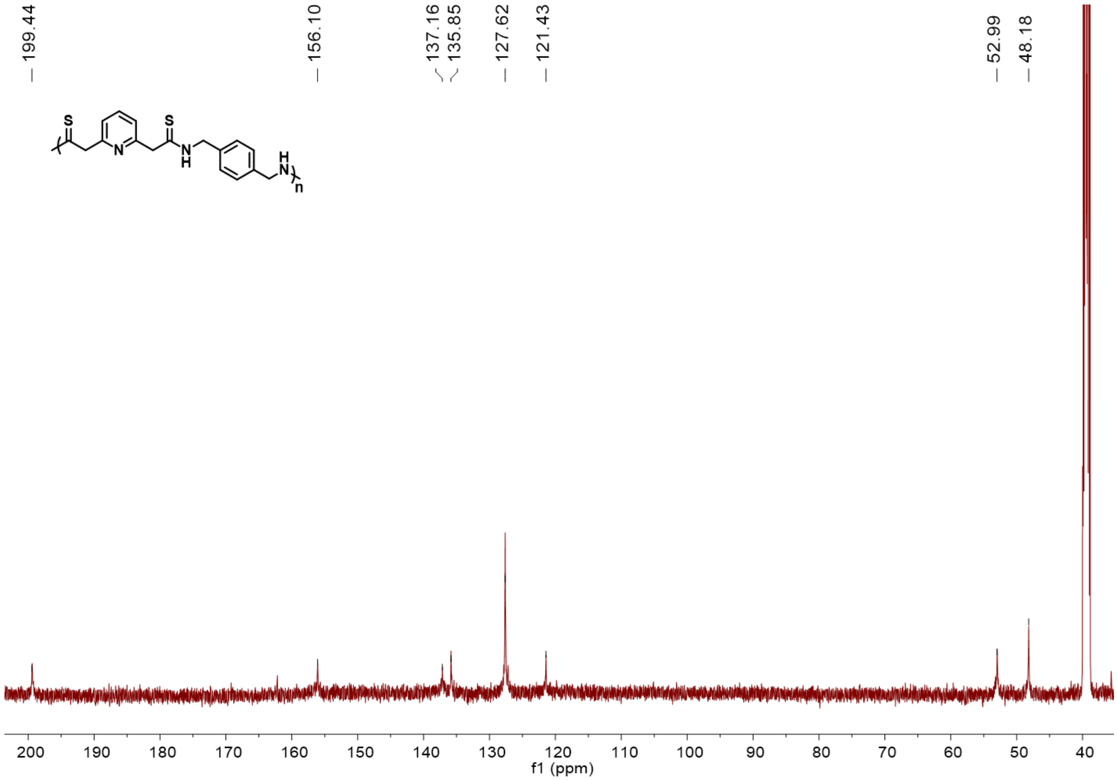

Fig. S16 ^{13}C NMR spectrum of P**1** in DMSO-d_6.

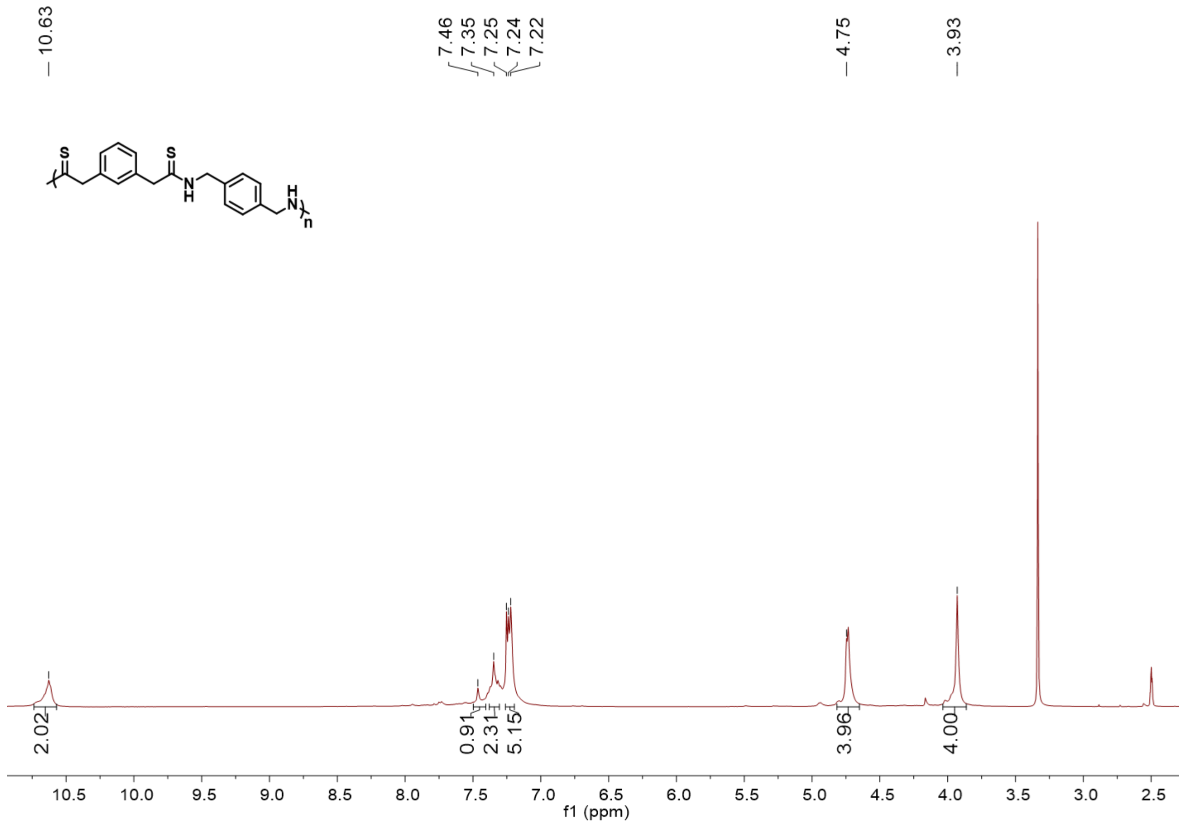

Fig. S17 ^{1}H NMR spectrum of P**2** in DMSO-d_6.

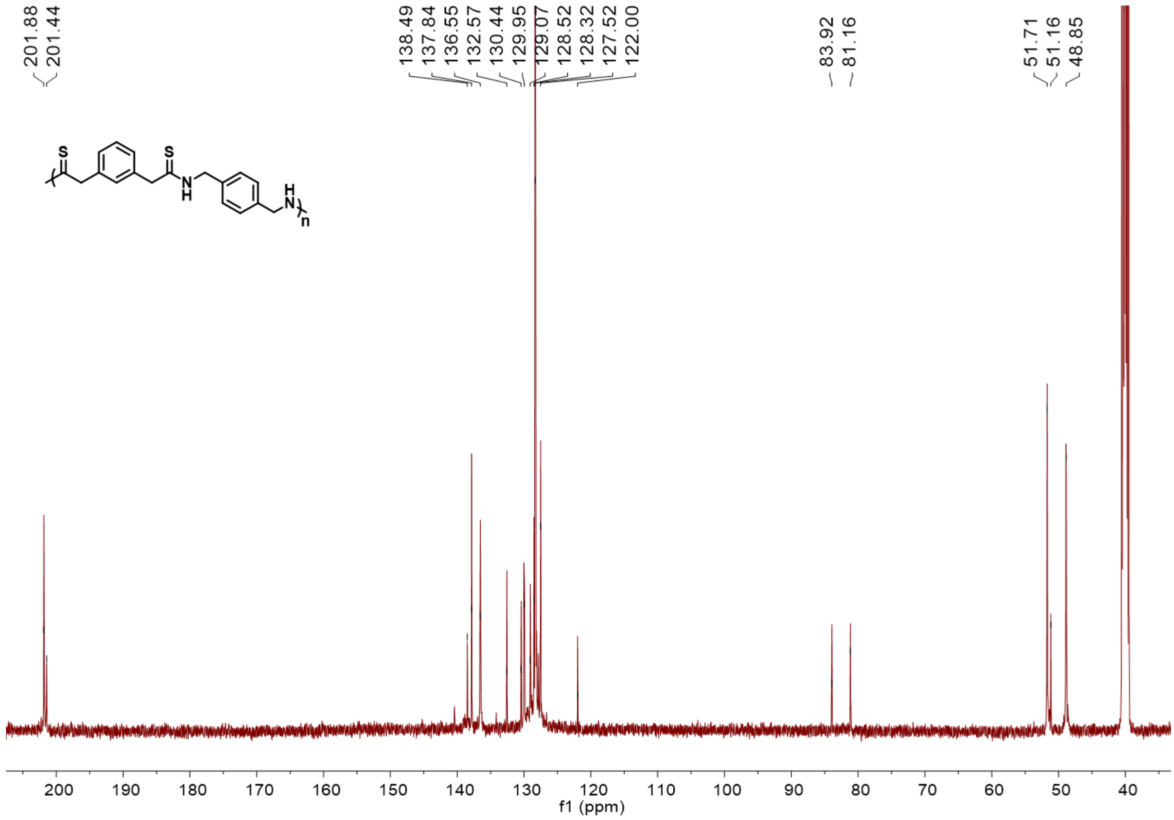

Fig. S18 ^{13}C NMR spectrum of P**2** in DMSO-d_6.

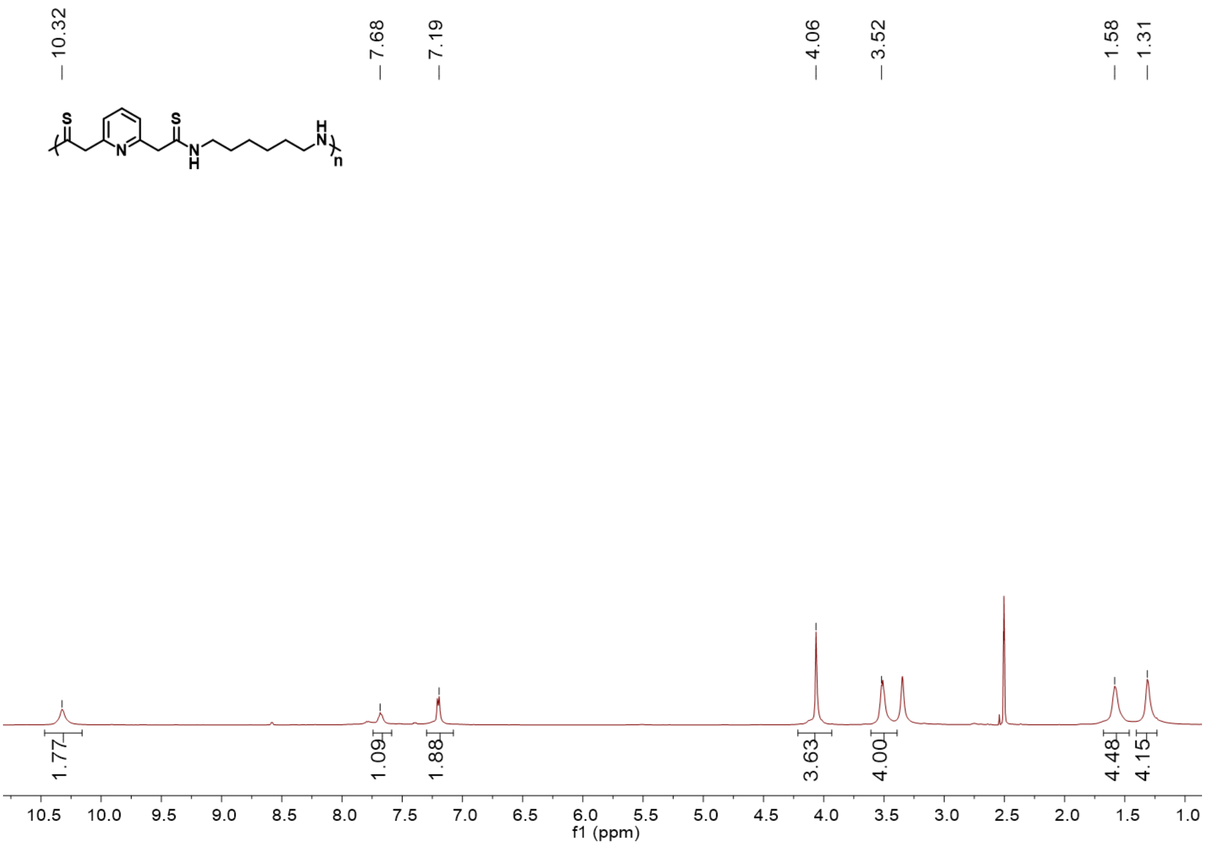

Fig. S19 ^{1}H NMR spectrum of P**3** in DMSO-d_6.

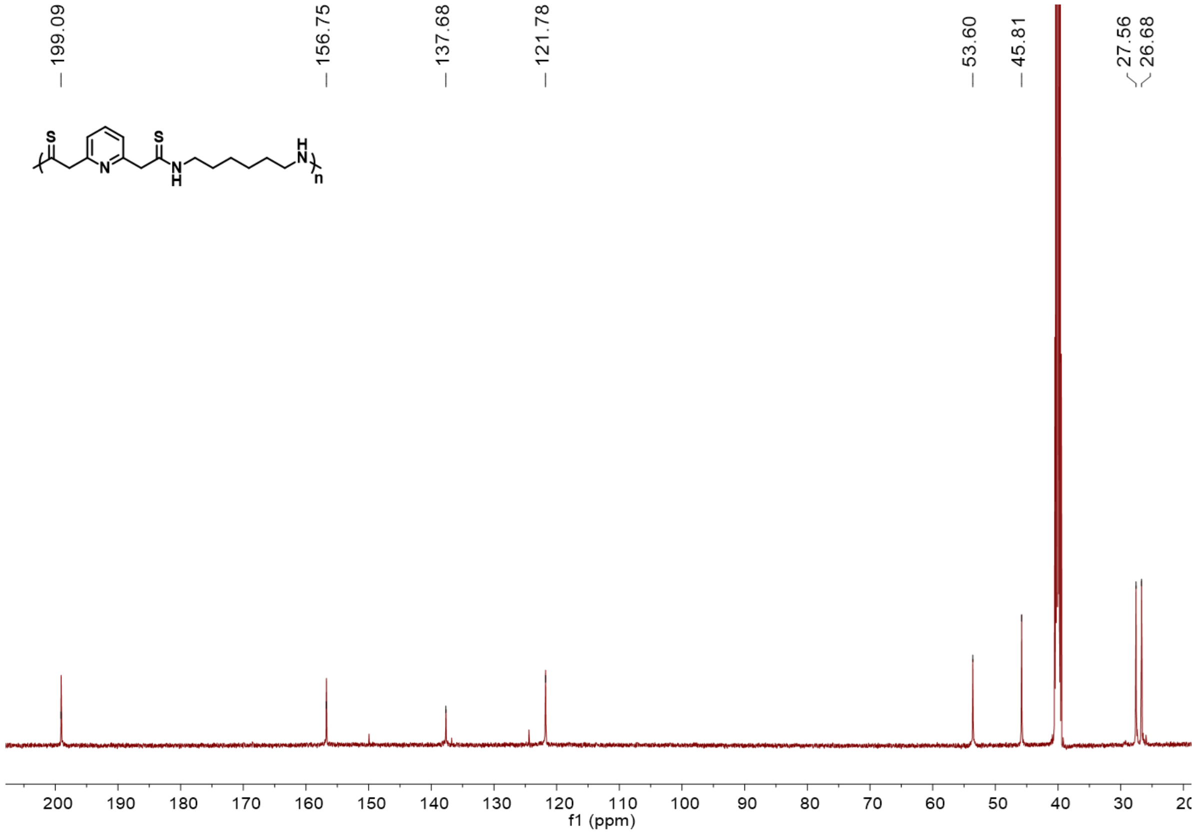

Fig. S20 ^{13}C NMR spectrum of P**3** in DMSO-d_6.

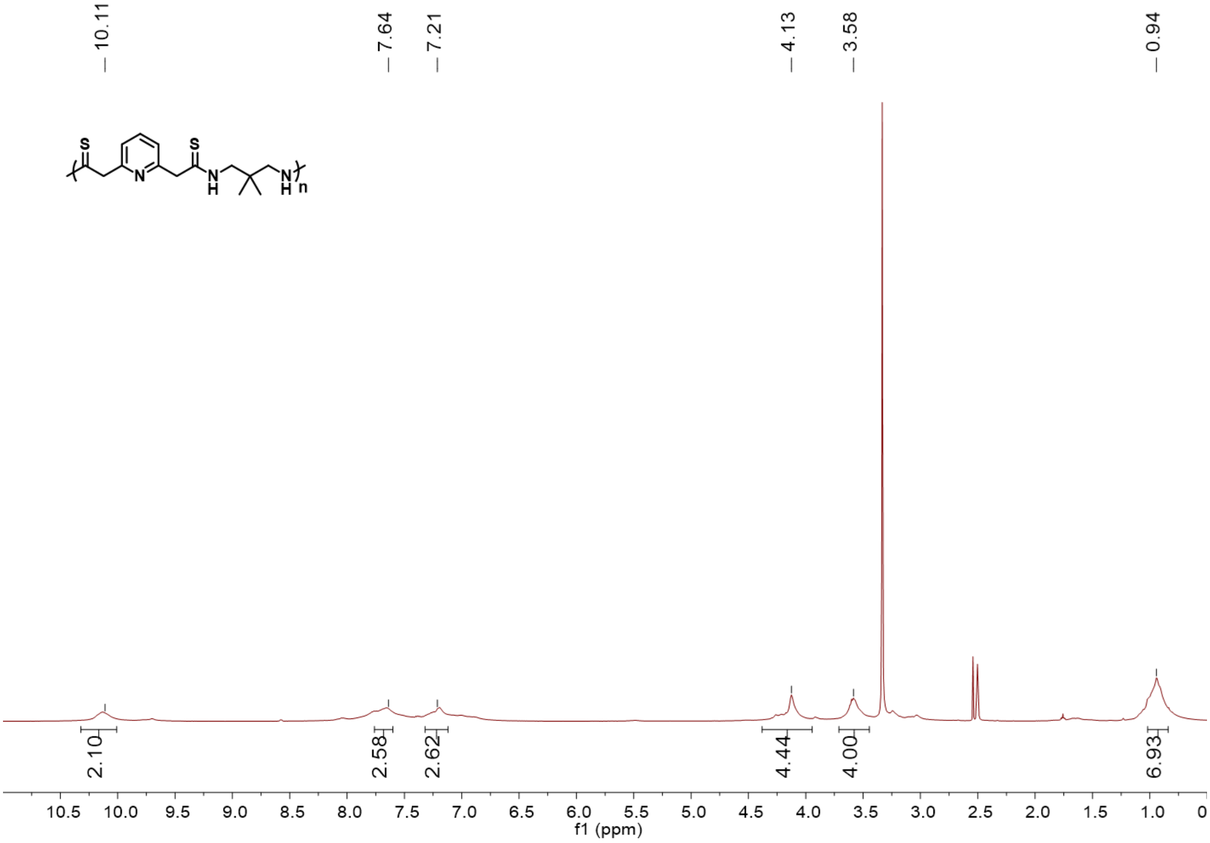

Fig. S21 ^{1}H NMR spectrum of P**4** in DMSO-d_6.

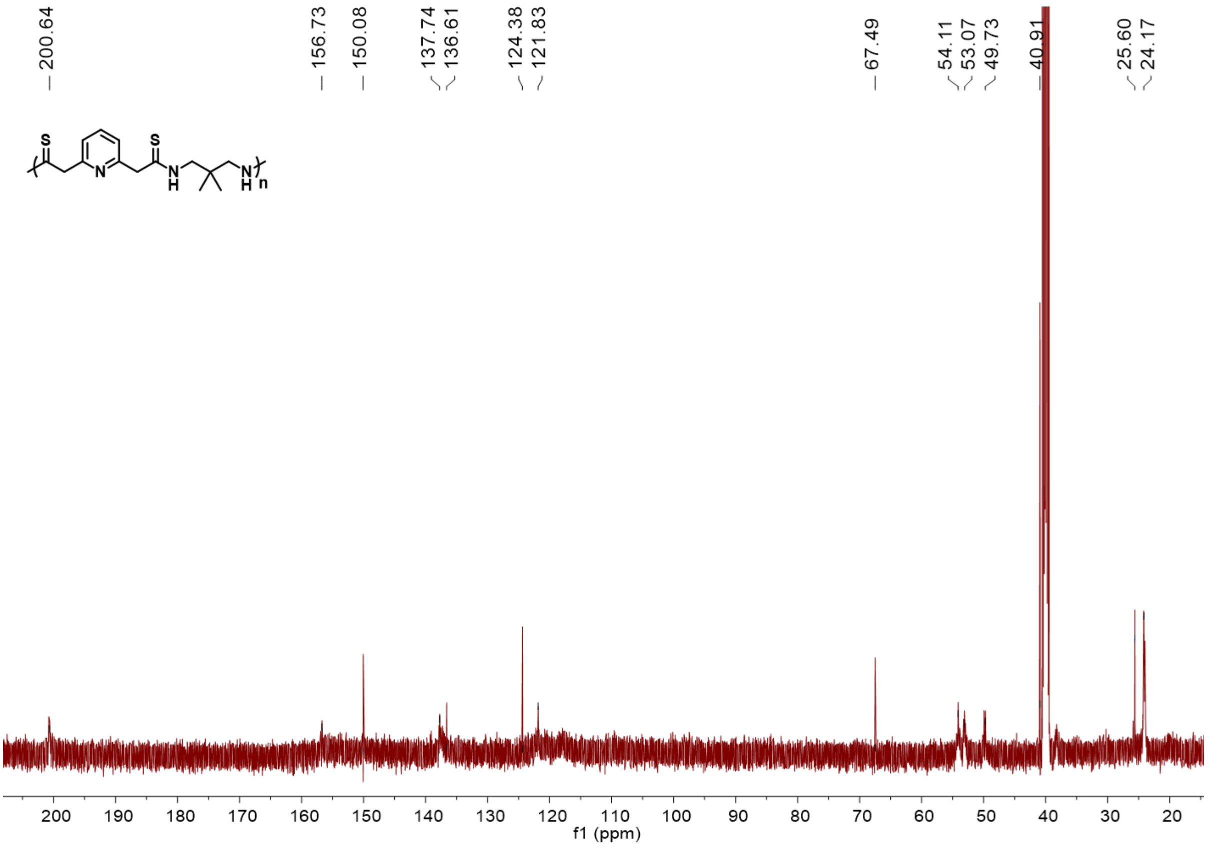

Fig. S22 ^{13}C NMR spectrum of P**4** in DMSO-d_6.

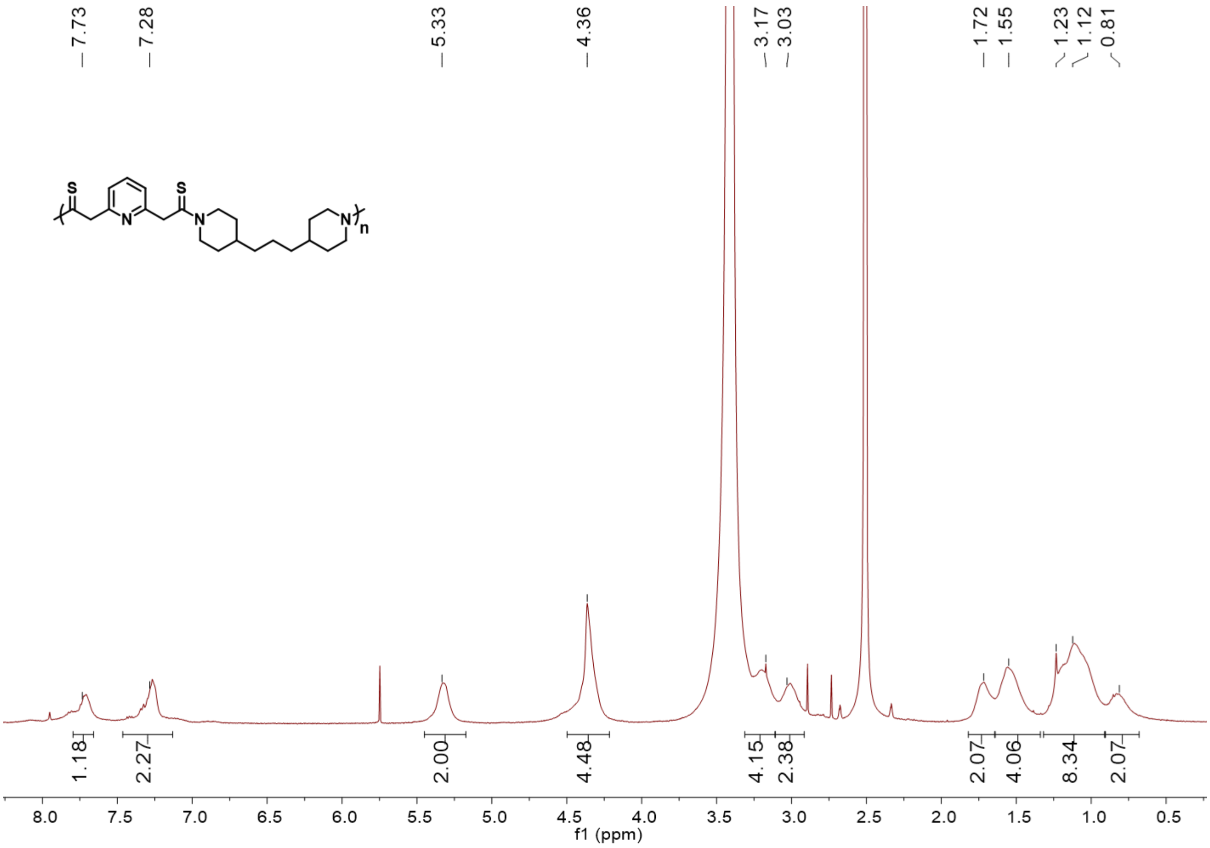

Fig. S23 ^{1}H NMR spectrum of P**5** in DMSO-d_6.

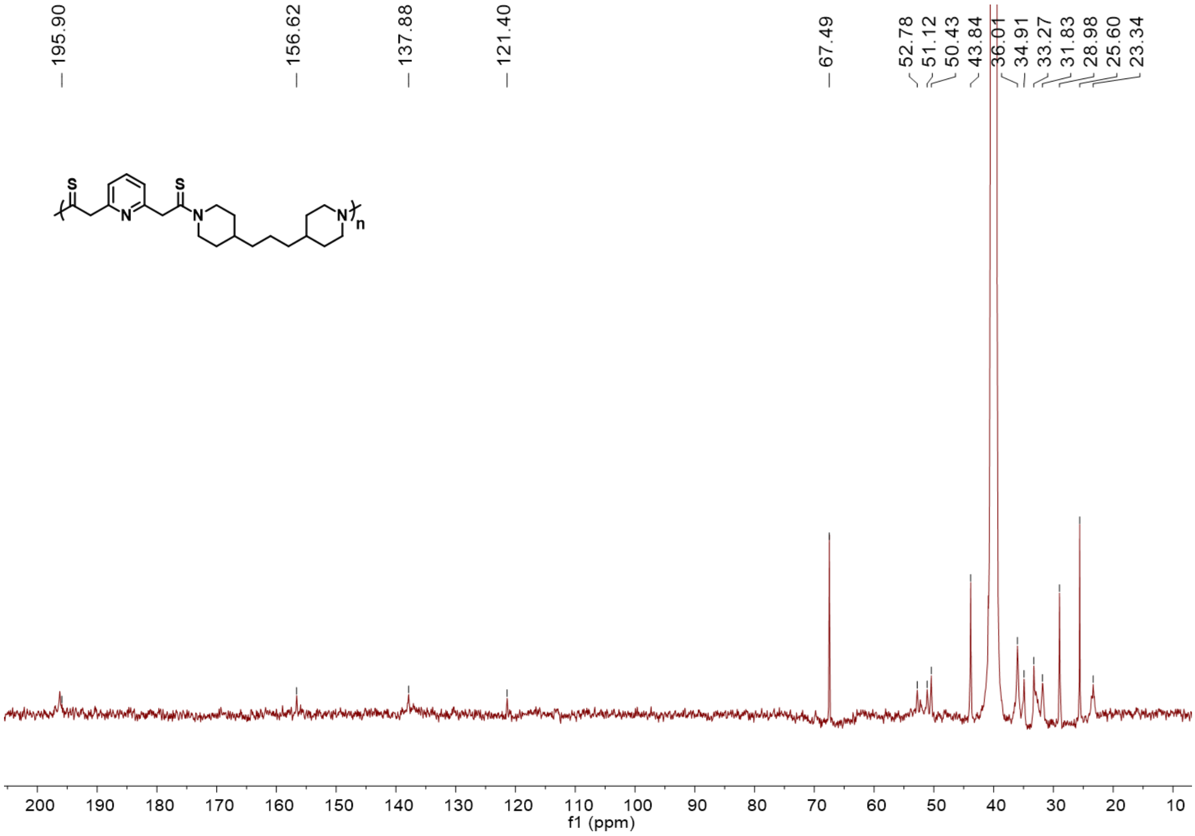

Fig. S24 ^{13}C NMR spectrum of P**5** in DMSO-d_6.

References

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