Electronic Supplementary material (ESI) for Polymer Chemistry

Synthesis of thioamide containing polybenzoxazines by the Willgerodt–Kindler Reaction

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Contents:

Synthesis of Bis(VaBz)-Hex

In a 500 ml round-bottom flask, 4-hydroxy-3-methoxybenzaldehyde (vanillin) (30g, 0.197 mol), 1,6-diaminohexane (11.457g, 0.0986 mol) and paraformaldehyde (11.842 g, 0.394 mol) were added in 250 ml chloroform. The mixture was magnetically stirred under reflux for 24 h. After cooling the content of the flask, the solution was extracted with 0.3 M sodium hydroxide for five times (V_{total} = 1000 mL). Then, to neutralize the solution, chloroform solution was washed with distilled water (V_{total} = 500 mL) for three times. The solution was dried with anhydrous Na_2SO_4 and then filtered. Chloroform was evaporated with a rotary. Then the remaining product was dried under vacuum at 40 °C for 24 h. (Yield: *ca.* 36%)

Attempt to synthesize of main chain polybenzoxazine precursors

Typical procedure as follows: 1,6-diaminohexane (20 mmol, 0.2324 g) (or Jeffamine ED900 (20 mmol , 1.8g)), elemental sulfur (5 mmol, 0.160 g) were added in 10 mL DMAc in round bottom flask under nitrogen gas. After stirring the content for 20 min., Bis(VaBz)-Hex (20 mmol, 0.937g, dissolved in 7 mL DMAc) was added into the mixture. The whole mixture heated at 100 °C for 6h under nitrogen blanket. Then, the reaction content was cooled down to ambient temperature and poured into methanol (*ca.* 100 mL) dropwise. After keeping the MeOH solution in a refrigerator for 24 h, precipitated product (polymer) was filtered and washed with cold methanol. The polymer was dried at ambient temperature in a vacuum chamber for 24 h.

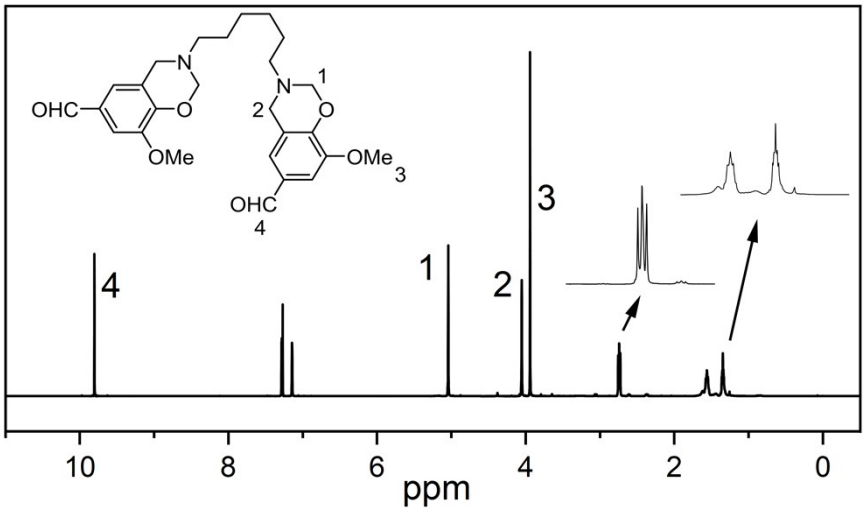


Figure S1: ^{1}H NMR spectrum of Bis(VaBz)-Hex

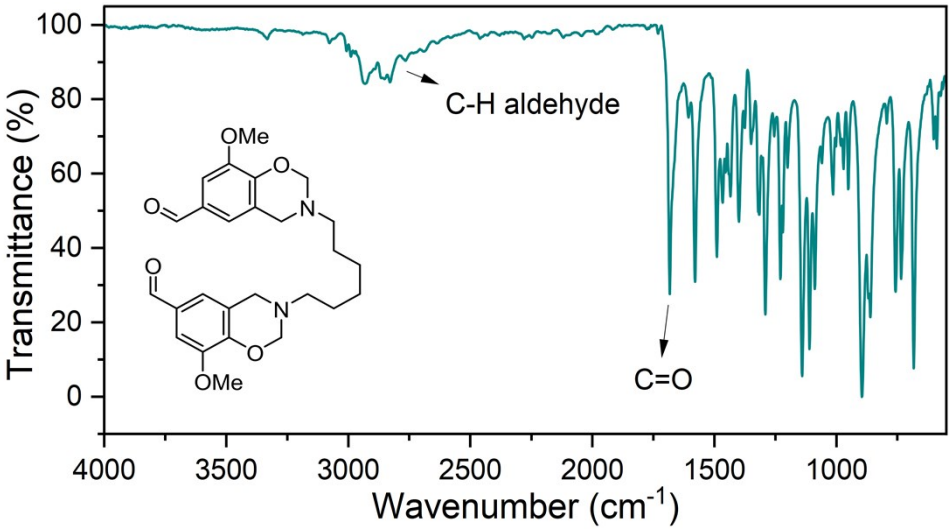


Figure S2: FTIR spectrum of Bis(VaBz)-Hex

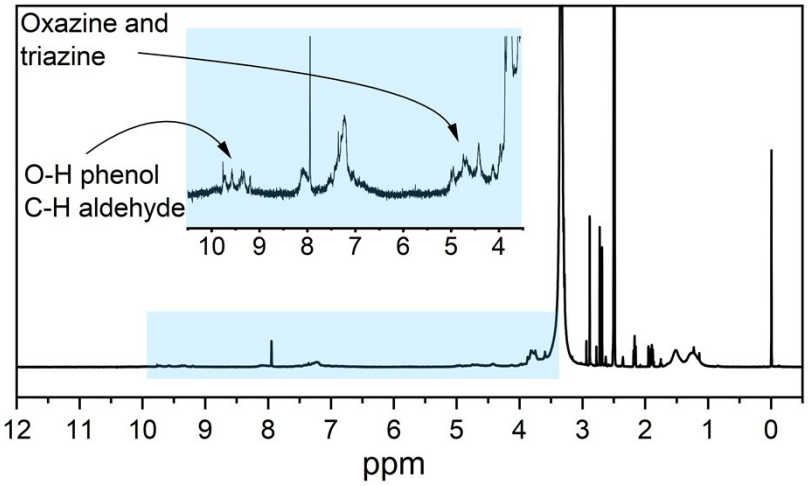


Figure S3: ^{1}H NMR spectrum of the DMSO-d_6 soluble sample from one-pot main chain polybenzoxazine synthesis experiment

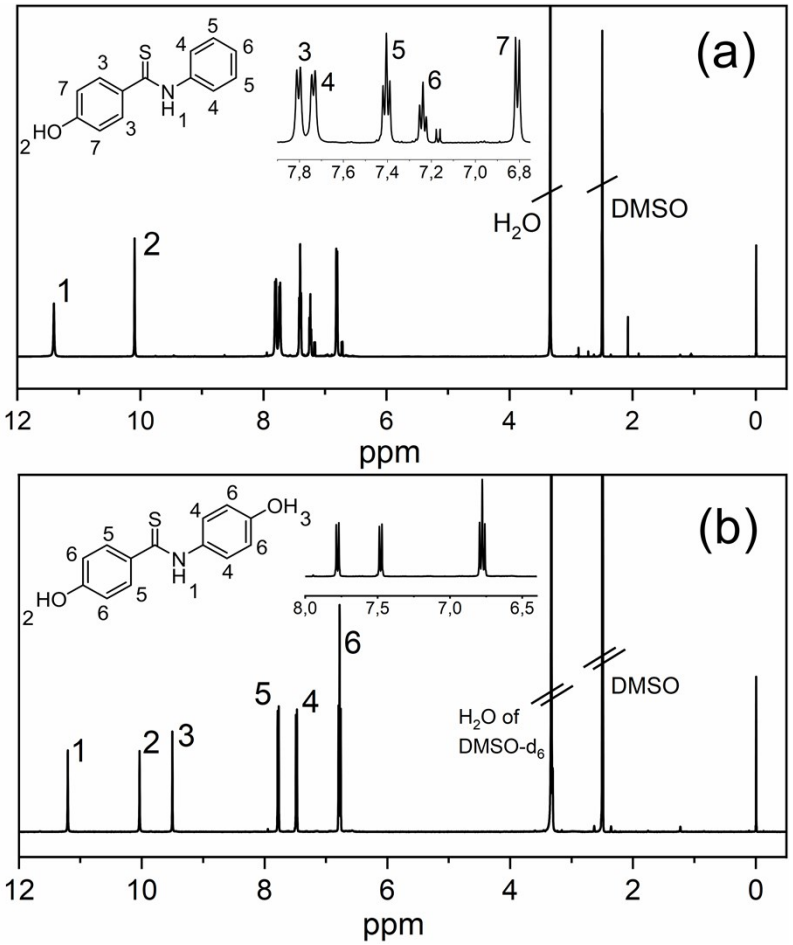


Figure S4: ^{1}H NMR spectra of 4-hydroxy-*N*-phenylbenzothioamide (monohydroxythioamide) (a) and 4-hydroxy-*N*-(4-hydroxyphenyl)benzothioamide (dihydroxythioamide) (b)

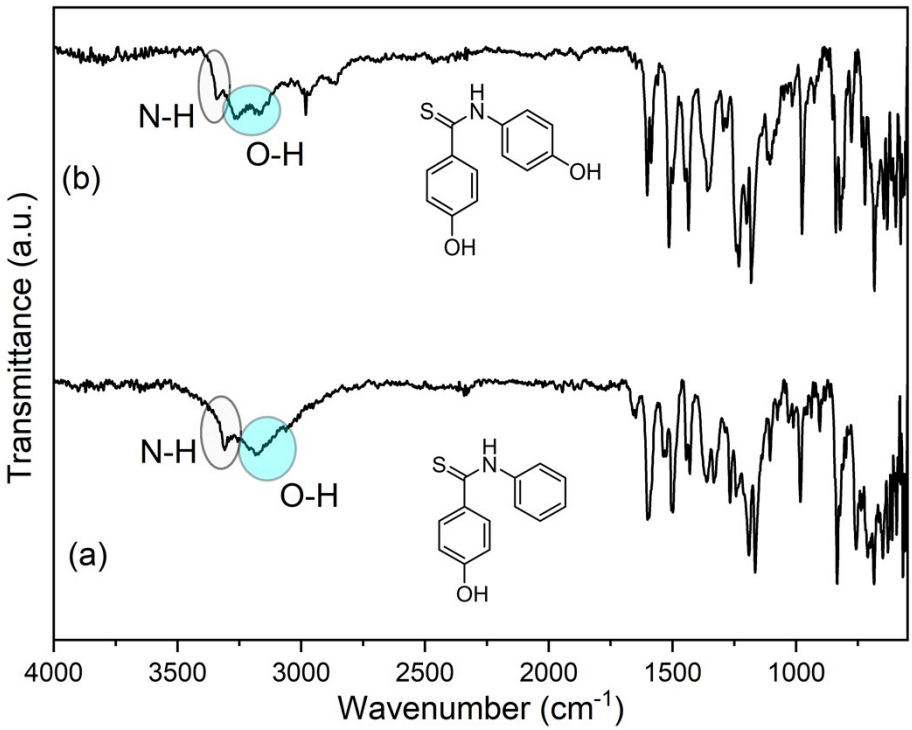


Figure S5: FTIR spectra of monohydroxythioamide (a) and dihydroxythioamide (b).

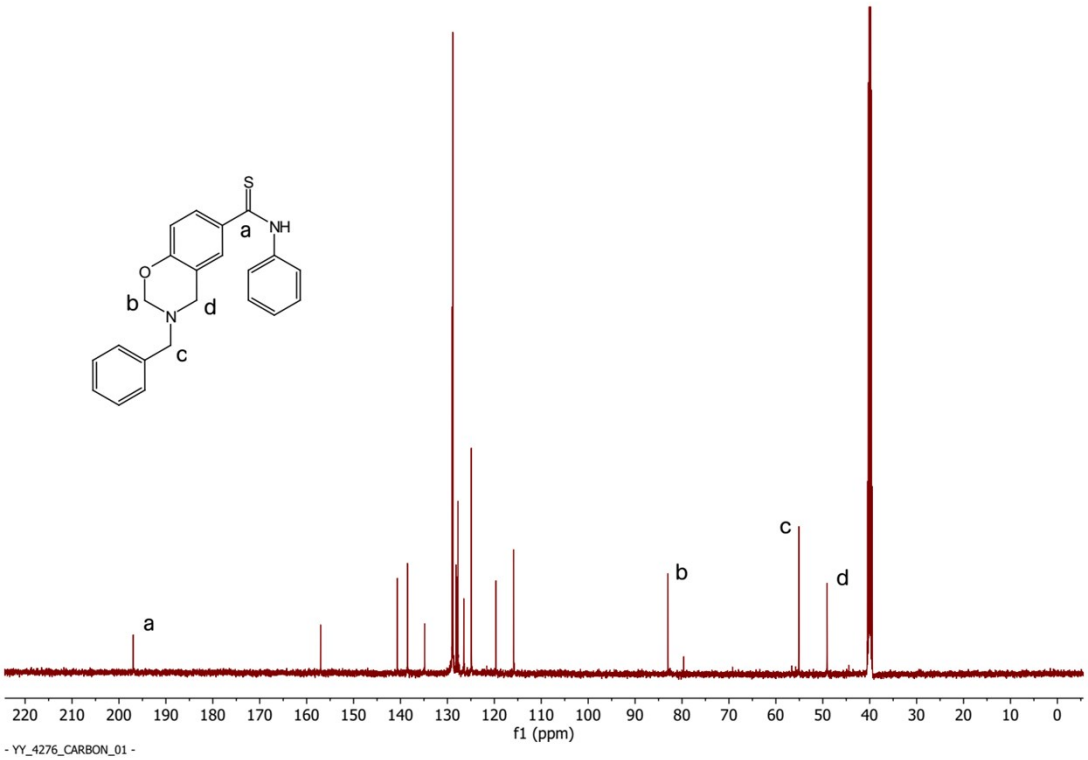


Figure S6: ^{13}C NMR spectrum of Th-amd-MonoBz-Bn

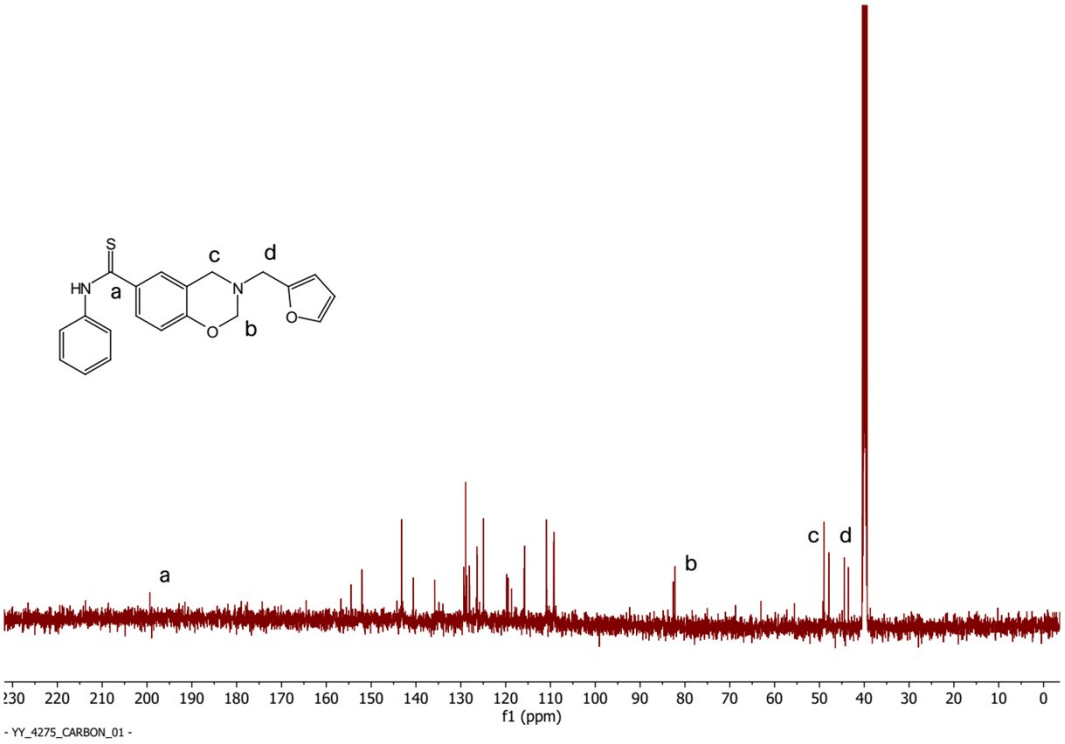


Figure S7: ^{13}C NMR spectrum of Th-amd-MonoBz-Fr

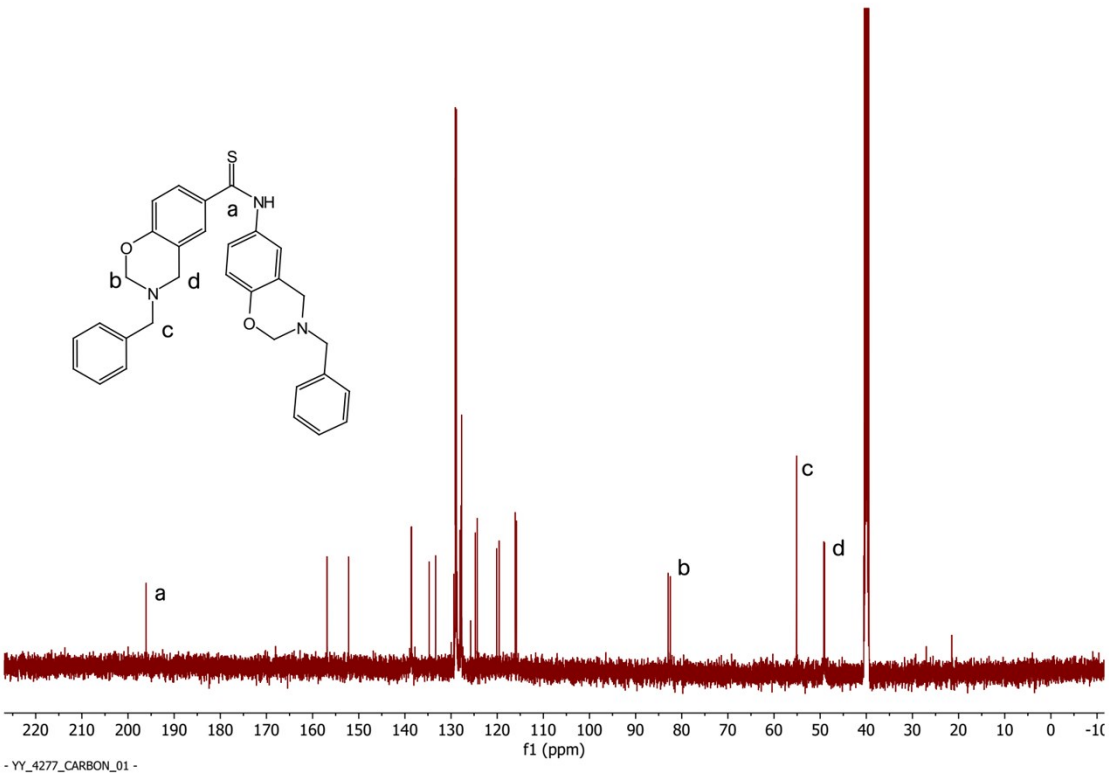


Figure S8: ^{13}C NMR spectrum of Th-amd-DiBz-Bn

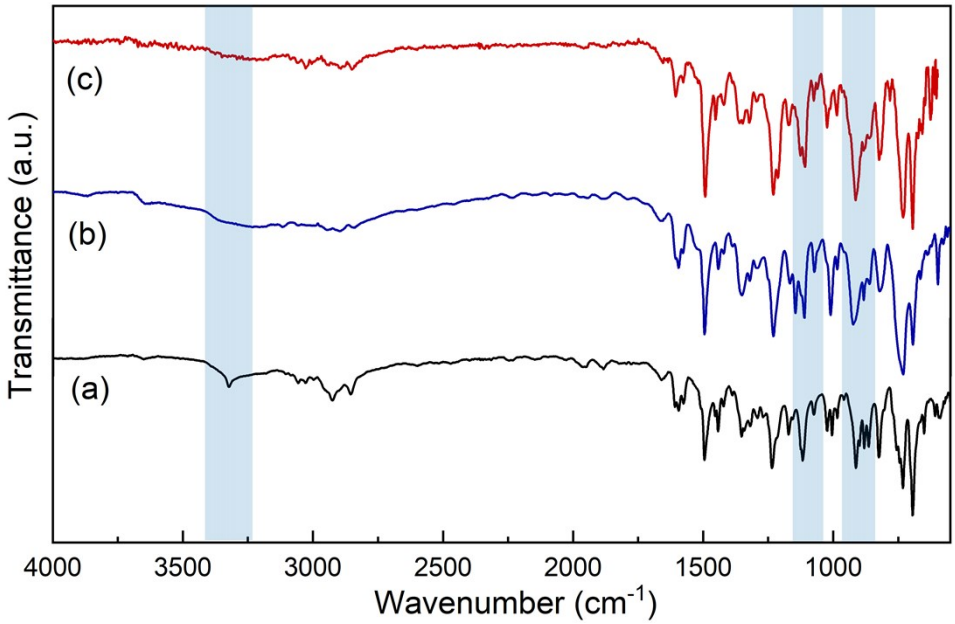
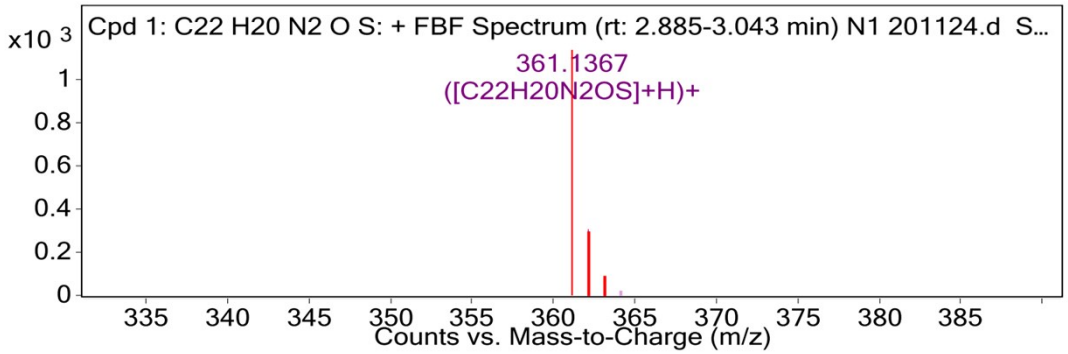


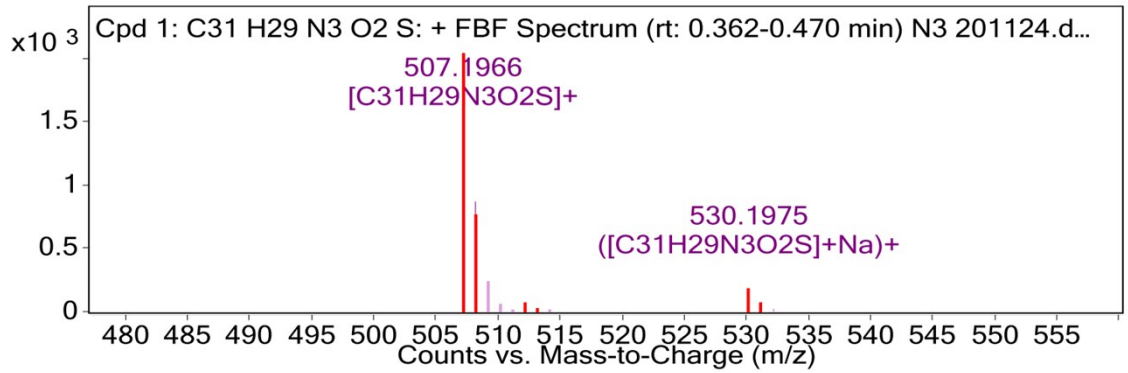
Figure S9: FTIR spectra of Th-amd-MonoBz-Bn (a), Th-amd-MonoBz-Fr (b), Th-amd-DiBz-Bn (c).



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
361,1367	1	1140,71	C22H20N2OS	(M+H)+
362,139	1	307,86	C22H20N2OS	(M+H)+
363,1299	1	56,06	C22H20N2OS	(M+H)+

Figure S10: LS/MS results with MS Spectrum Peak List for Th-amd-MonoBz-Bn



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
507,1966	1	2041,8	C31H29N3O2S	M+
508,1986	1	869,27	C31H29N3O2S	M+
512,1753	1	63,53	C31H29N3O2S	(M+Na)+[-H2O]
513,1882	1	22,77	C31H29N3O2S	(M+Na)+[-H2O]
530,1975	1	164,07	C31H29N3O2S	(M+Na)+
531,2128	1	74,95	C31H29N3O2S	(M+Na)+

Figure S11: LS/MS results with MS Spectrum Peak List for Th-amd-DiBz-Bn

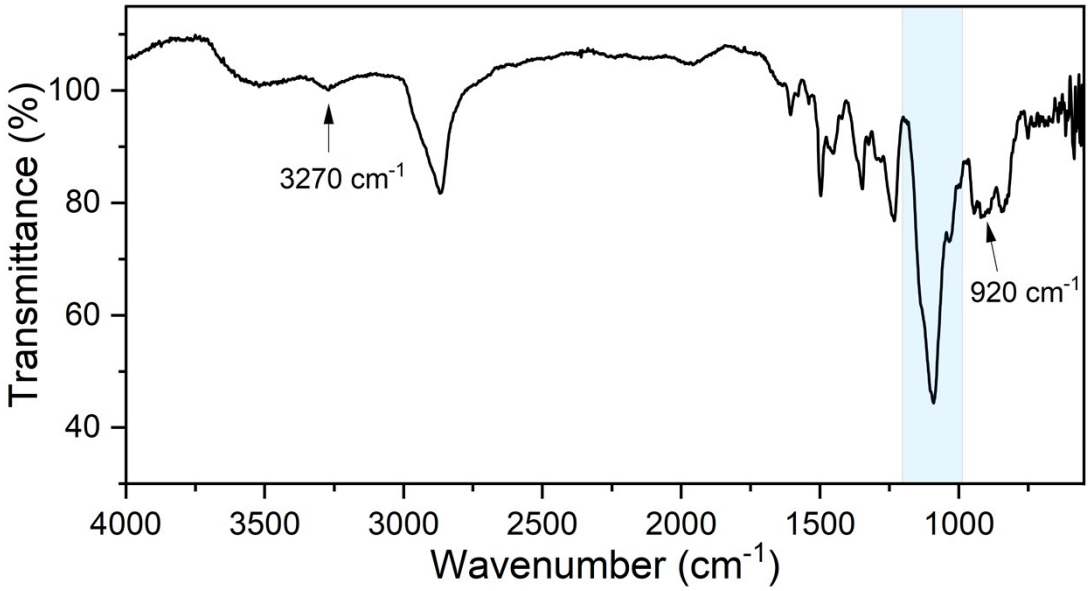


Figure S12: FTIR spectrum of poly(thioamide-benz-PPEO)

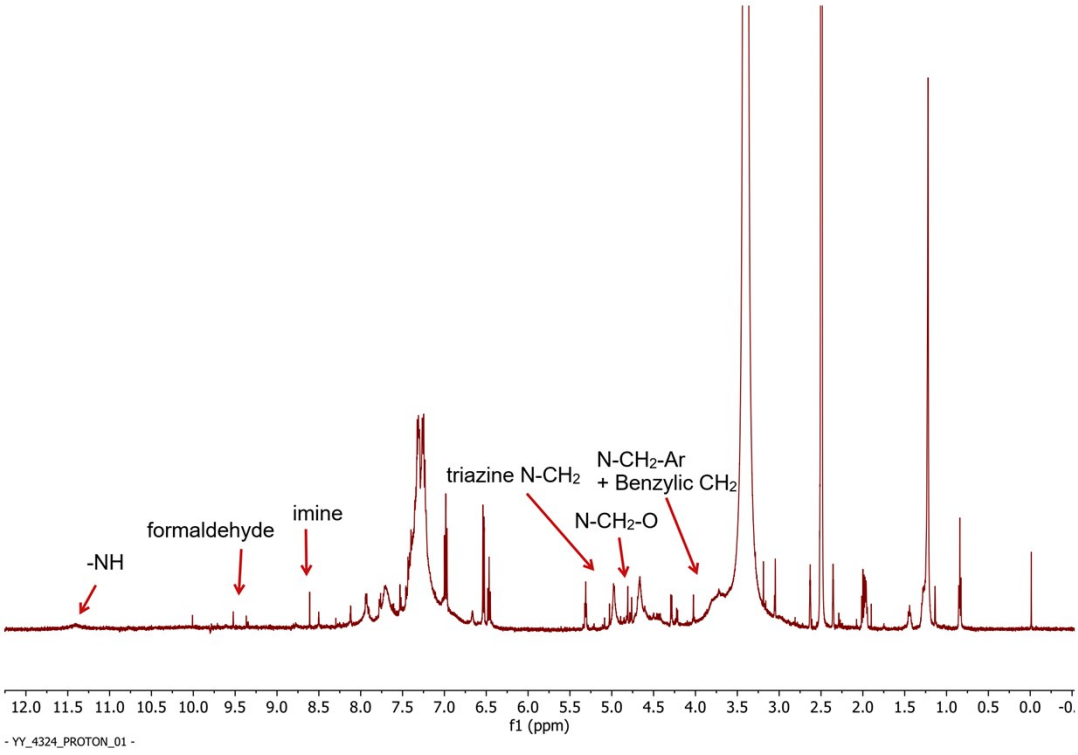


Figure S13: ^{1}H NMR spectrum of extracted sample from cured Th-amd-MonoBz-Bn