Supplementary Information (SI) for ChemComm.

Supporting Information

Copper-Catalyzed Multicomponent Polymerization of Elemental Selenium for Regioselective Synthesis of Poly(5-diselenide-triazole)s

Yangyang Yue,[a] Chen Qu,[a] Nan Zheng,[a] Yubin Zheng,[b,]* Wangze Song[a,]*

[a] Central Hospital of Dalian University of Technology, School of Chemistry, Dalian University of Technology, Dalian, 116024, P. R. China.

[b] Dalian University of Technology Corporation of Changshu Research Institution, Suzhou, 215500, P. R. China

Corresponding Authors:
E-mail: wzsong@dlut.edu.cn (W. S.)
E-mail: zybwl@163.com (Y. Z.)

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1. General Methods.

Materials

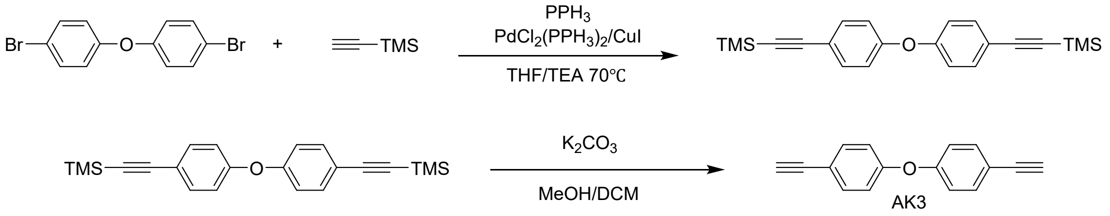
Bis(4-bromophenyl) ether (Energy Chemical, 98%), 9,10-Dibromoanthracene (Energy Chemical, 98%), 2,6-Dibromonaphthalene (Energy Chemical, 98%), 3-Ethynylthiophene (Aladdin, 97%), Phenylacetylene (Energy Chemical, 96%), Phenyl(prop-2-yn-1-yl)sulfane (Energy Chemical, 98%), Benzyl azide (Energy Chemical, 98%), α-Bromodiphenylmethane (Energy Chemical, 95%), Triphenylphosphine (Energy Chemical, 97%, PPh_3), bis(triphenylphosphine)palladium(II) chloride (Energy Chemical, 97%, $PdCl_2(PPh_3)_2$), trimethylsilylacetylene (Energy Chemical, 97%), 4,4'-diiodo-1,1'-biphenyl (Energy Chemical, 97%), 4-dimethylaminopyridine (Energy Chemical, 97%, DMAP), β-Phenylethyl bromide (Energy Chemical, 98%), N-(4-Bromobutyl)phthalimide (Energy Chemical, 98%), 1,4-Bis(bromomethyl)benzene (Energy Chemical, 98%), 1,4-diethynyl benzene (MACKLIN, 97%), 4-Methoxybenzylchloride (MACKLIN, 98%), were used without further purification. All the solvents including tetrahydrofuran (THF), dichloromethane (DCM), N,N-dimethylformamide (DMF), diethyl ether, methanol (MeOH), toluene, dimethyl sulfoxide (DMSO), ethyl acetate (EtOAc) and chloroform ($CHCl_3$) were dried by a column packed with 4 Å molecular sieves before use. Thin layer chromatography was performed using pre-coated silica gel plates and visualized with UV light at 254 nm. Flash column chromatography was performed with silica gel (40-60 μm).

Characterization.

^1H nuclear magnetic resonance spectra (NMR) were obtained on Bruker Avance II 400 MHz, Bruker Avance III 500 MHz and Bruker Avance III 600 MHz recorded in ppm (δ) downfield of TMS (δ = 0) in $CDCl_3$ or DMSO-d_6 unless noted otherwise. Signal splitting patterns were described as singlet (s), doublet (d), triplet(t), quartet (q), quintet (quint), or multiplet (m), with coupling constants (J) in hertz (Hz). The number-average molecular weight (M_n) and polydispersity index ($Đ$) of polymers were determined by gel permeation chromatography (GPC) equipped with an isocratic pump (model 1515, Waters Corporation) and a refractive index (RI) detector (model 2414, Waters Corporation). Separations were performed at 50 °C using PLgel PL1110-6530/6540 columns (Agilent, the molecular weight upper limit was 450,000 g/mol) and DMF containing 0.1 M LiBr as the mobile phase. PS with M_ns ranging from 1460 g/mol to 252,200 g/mol were used as the standards. X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB XI$^+$. Mass spectrometry tests are performed on orbitrap Liquid Chromatography-Mass Spectrometry. FTIR Spectromter was conducted on an Nicolet 6700.

2. Synthesis of monomer AK2-5.

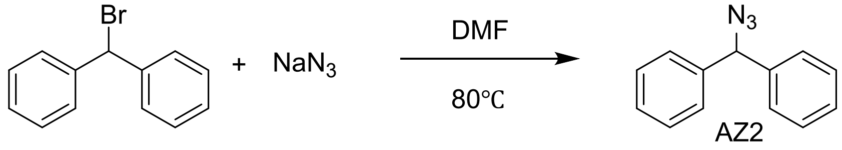
Monomer AK2-5 were prepared according to the literature procedure.[1] AK3 was used as typical example.



4,4'-Oxybis(ethynylbenzene) (AK3): $PdCl_2(PPh_3)_2$ (701.9 mg, 1 mmol), CuI (380.9 mg, 2 mmol), Bis(4-bromophenyl) ether (3.28 g, 10 mmol) were added into a 250 mL two-necked round bottom flask, and dissolved with 60 mL triethylamine and 10 mL distilled THF under nitrogen. After addition of trimethylsilylacetylene (5.65 mL, 40 mmol), the mixture was refluxed for 12 h. After evaporating the solvent and purified by silica gel column chromatography using petroleum as eluent, white solid of TMS protected product was obtained. The above solid was dissolved together with KOH (3.366 g, 60 mmol) in DCM and methanol, and stirred at room temperature for 4 h. A white solid of AK3 can be obtained after purification by silica gel column chromatography using PE as eluent (yield 83%).

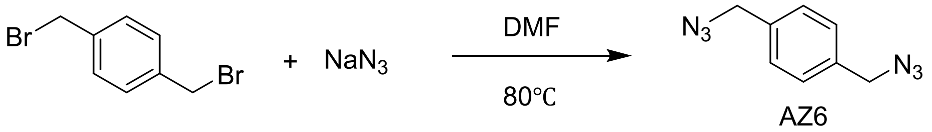
3. Synthesis of monomer AZ1-5.

Monomer **AZ1-5** were prepared according to the literature procedure.[2] **AZ2** was used as typical example.



AZ2 was used as typical example. NaN3 (97.5 mg, 1.5 mmol, 1.5 eq.) was added into a stirred solution of halide (246 mg, 1 mmol, 1 eq.) in DMF (1.25 mL). The reaction was heated to 80 °C and the mixture was stirred for 12 h. The reaction mixture was quenched with H_2O (5 ml), extracted with EtOAc and dried over Na_2SO_4. The solvent was evaporated under vacum to afford a colorless oil AZ2.

4. Synthesis of monomer AZ6.

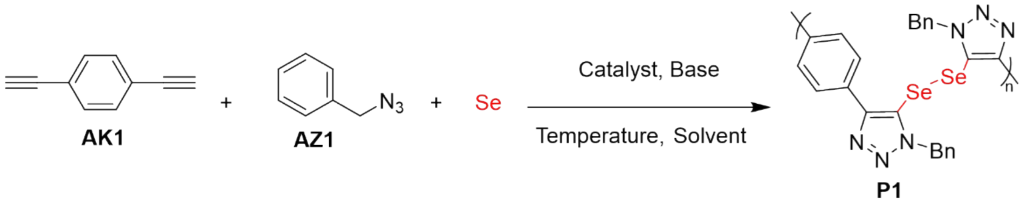


AZ6 was used as typical example. NaN3 (162.5 mg, 2.5 mmol, 2.5 eq.) was added into a stirred solution of 1,4-Dibromomethylbenzene (264 mg, 1 mmol, 1 eq.) in DMF (1.25 mL). The reaction was heated to 65 °C and the mixture was stirred for 12 h. The reaction mixture was quenched with H_2O (5 ml), extracted with EtOAc and dried over Na_2SO_4. The solvent was evaporated under vacum to afford a colorless oil AZ6.

5. Conditional Screening.

To obtain the soluble polymer with a high M_n and yield, **AK1**, **AZ1**, and **Se** were selected as model monomers to optimize the polymerization conditions (Table 1). The experiment was initially conducted in the mixture solvent such as dioxane/H_2O, DMF/ H_2O, and $CHCl_3$/H_2O (V:V = 1:1) at room temperature (Table 1, entries 1-3). The improvements of yield and M_n were observed using chloroform and water as solvent (Table 1, entry 3). We were delighted to find that both yield and M_n of poly(5-diselenide-triazole) **P1** were increased to 72% and 12,400 g/mol at 50 °C with excellent regioselectivity (Table 1, entry 4). Then, other copper catalysts besides $Cu(MeCN)_4PF_6$ were screened. It was found that both Cu(I) including $Cu(MeCN)_4BF_4$, CuCl and CuI, and even Cu(II) such as $CuCl_2$ and $Cu(OAc)_2$ could well promote such MCP to afford desired polymer **P1** with good yield and M_n (Table 1, entries 5-9). Among above copper catalysts, CuI was selected as the best catalyst for further optimization due to affording high M_n of 13,900 g/mol and 81% yield (Table 1, entry 7). Better results (83% yield and 25,300 g/mol M_n) were attained using 5 mol% CuI catalyst loading instead of 10 mol% and 20 mol% (Table 1, entries 10-11). Therefore, 5 mol% CuI was used for further optimization. Various bases including Cs_2CO_3, triethylamine (TEA), *N*, *N*-diisopropylethylamine (DIPEA), 4-dimethylaminopyridine (DMAP), K_2CO_3, and KOH were examined (Table 1, entries 12-16). Among above bases, Cs_2CO_3 was demonstrated to be the best choice. The equivalents of Cs_2CO_3 were further optimized. When 1.0 equiv of Cs_2CO_3 was used instead of 3 equiv, the yields and M_n of products dropped dramatically (Table 1, entry 17). Continuously increasing base to 6.0 equiv would give an optimal yield (86%) and M_n (41,700 g/mol) for polymer **P1** (Table1, entry18).

Table 1. Optimization of the Polymerization Conditions for MCP of AK1, AZ1, and elemental selenium.[a]



Entry	Catalyst	Loading (mol%)	Base	Temperature (°C)	Solvent (V:V = 1:1)	Yield (%)	M_n (g/mol)[b]	$Đ$[b]
1	$Cu(MeCN)_4PF_6$	10	Cs_2CO_3	rt	dioxane/H_2O	65	4500	1.02
2	$Cu(MeCN)_4PF_6$	10	Cs_2CO_3	rt	DMF/ H_2O	61	4500	1.01
3	$Cu(MeCN)_4PF_6$	10	Cs_2CO_3	rt	$CHCl_3/H_2O$	70	4800	1.03
4	$Cu(MeCN)_4PF_6$	10	Cs_2CO_3	50	$CHCl_3/H_2O$	72	12400	1.53
5	$Cu(MeCN)_4BF_4$	10	Cs_2CO_3	50	$CHCl_3/H_2O$	74	8800	1.15
6	CuCl	10	Cs_2CO_3	50	$CHCl_3/H_2O$	74	9400	1.36
7	CuI	10	Cs_2CO_3	50	$CHCl_3/H_2O$	81	13900	1.41
8	$CuCl_2$	10	Cs_2CO_3	50	$CHCl_3/H_2O$	71	12400	1.53
9	$Cu(OAc)_2$	10	Cs_2CO_3	50	$CHCl_3/H_2O$	69	10400	1.36
10	CuI	5	Cs_2CO_3	50	$CHCl_3/H_2O$	83	25300	1.14
11	CuI	20	Cs_2CO_3	50	$CHCl_3/H_2O$	45	6100	1.09
12	CuI	5	TEA	50	$CHCl_3/H_2O$	72	9300	1.26
13	CuI	5	DMAP	50	$CHCl_3/H_2O$	41	9900	1.13
14	CuI	5	DIPEA	50	$CHCl_3/H_2O$	62	45700	1.34
15	CuI	5	K_2CO_3	50	$CHCl_3/H_2O$	68	13900	1.41
16	CuI	5	KOH	50	$CHCl_3/H_2O$	68	34600	1.16
17[c]	CuI	5	Cs_2CO_3	50	$CHCl_3/H_2O$	22	5800	1.06
18[d]	**CuI**	**5**	**Cs_2CO_3**	**50**	**$CHCl_3/H_2O$**	**86**	**41700**	**1.16**

[a] Reaction conditions: **AK1** (0.1 mmol), **AZ1** (0.6 mmol), **Se** (1.2 mmol), copper catalyst, Me₄phen (6 mol%), base (3.0 equiv) and TBAB (tetrabutylammonium bromide) (1.0 equiv) in the mixture solvent of organic solvent with H_2O (V:V = 1:1, 1.0 mL) for 12 h. [b] M_n and $Đ$ were determined by gel permeation chromatography (GPC) in DMF with PS (polystyrene) standards. [c] 1.0 equiv Cs_2CO_3 as base was used. [d] 6.0 equiv Cs_2CO_3 as base was used.

6. General polymerization method using AKs, AZs and Se.

All the polymerizations were carried out in air as mentioned below using **AK1**, **AZ1** and **Se** as a typical example. In a 2 ml glass vial, **CuI** (0.005 mmol, 0.9 mg, 5 mol%), **Me$_4$phen** (0.006 mmol, 1.5mg, 6 mol%), were dissolved in $CHCl_3/H_2O$ (v/v=1/1, 1.0 ml), stirring for 5-10 min. **TBAB** (0.1 mmol, 32.2 mg, 1 equiv), **AK1** (0.1 mmol, 12.6 mg, 1 equiv.)， **AZ1** (0.6 mmol, 80.4 mg, 6 equiv.)， **Se** (1.2 mmol, 95 mg, 12 equiv.) and **CS$_2$CO$_3$** (0.6 mmol, 195.6 mg, 6 equiv) was then added. The mixture was stirred at 50℃ temperature for 12 h. The mixture was filtered through a microfiltration membrane. The filtrate was precipitated with 20 mL methanol. The products were washed with methanol for three times and collected by centrifugation. The polymer **P1** was dried in vacuo and characterized by ^{1}H NMR, ^{13}C NMR, and GPC.

P1(AK1/AZ1/Se) light yellow soild, 47.3 mg, yield: 86%, M_n = 41,700 g/mol, M_w = 48,500 g/mol, M_w/M_n = 1.16. ^{1}H NMR (500 MHz, DMSO) δ 7.93-7.19 (14H), 6.00-5.40 (4H). ^{13}C NMR (126 MHz, DMSO) δ 146.7, 136.4, 132.7, 129.3, 128.6, 128.3, 125.6, 122.4, 53.6.

P2(AK2/AZ1/Se) light yellow soild, 48.1 mg, yield: 77%, M_n = 39,100 g/mol, M_w = 49,900 g/mol, M_w/M_n = 1.27. ^{1}H NMR (500 MHz, DMSO) δ 8.22-7.30 (18H), 6.00-5.22 (4H). ^{13}C NMR (126 MHz, DMSO) δ 146.8, 139.7, 136.0, 132.9, 129.3, 128.7, 128.4, 127.4, 126.2, 122.2, 53.5.

P3(AK3/AZ1/Se) light yellow soild, 48.8 mg, yield: 76%, M_n = 11,300 g/mol, M_w = 15,700 g/mol, M_w/M_n = 1.38. ^{1}H NMR (500 MHz, DMSO) δ 7.63-6.92 (18H), 6.00-5.22 (4H). ^{13}C NMR (126 MHz, DMSO) δ 157.0, 134.2, 131.7, 129.7, 129.3, 128.6, 128.3, 127.5, 122.0, 119.3, 53.8.

P4(AK4/AZ1/Se) light yellow soild, 58.5 mg, yield: 90%, M_n = 12,700 g/mol, M_w = 21,600 g/mol, M_w/M_n = 1.70. ^{1}H NMR (500 MHz, DMSO) δ 8.76-6.98 (18H), 6.37-5.62 (4H). ^{13}C NMR (126 MHz, DMSO) δ 142.9, 136.9, 131.5, 130.8, 129.7, 129.4, 128.7, 128.4, 127.4, 127.0, 53.6.

P5(AK5/AZ1/Se) light yellow soild, 47.4 mg, yield: 79%, M_n = 71,300 g/mol, M_w = 82,000 g/mol, M_w/M_n = 1.15. ^{1}H NMR (500 MHz, DMSO) δ 8.73-7.23 (16H), 6.11-5.15 (4H). ^{13}C NMR (126 MHz, DMSO) δ 150.2, 137.7, 135.9, 136.0, 132.0, 129.2, 128.4, 127.1, 126.5, 120.4, 53.6.

P6(AK1/AZ2/Se) light yellow soild, 59.5mg, yield: 85%, M_n = 34,900 g/mol, M_w = 43,000 g/mol, M_w/M_n = 1.23. ^{1}H NMR (500 MHz, DMSO) δ 8.84-7.06 (24H), 7.03-6.69 (2H). ^{13}C NMR (126 MHz, DMSO) δ 139.0, 129.5, 129.2, 129.0, 128.9, 128.8, 128.5, 127.6, 67.4.

P7(AK1/AZ3/Se) light yellow soild, 51.9mg, yield: 85%, M_n = 32,200 g/mol, M_w = 36,100 g/mol, M_w/M_n = 1.12. ^{1}H NMR (500 MHz, DMSO) δ 7.96-6.91 (12H), 5.93-5.17 (4H), 3.93-3.42 (6H). ^{13}C NMR (126 MHz, DMSO) δ 159.7, 146.8, 130.6, 130.1, 128.3, 126.4, 121.8, 114.6, 55.6, 53.1.

P8(AK1/AZ4/Se) light yellow soild, 46.4mg, yield: 80%, M_n = 38,300 g/mol, M_w = 45,600 g/mol, M_w /M_n = 1.28. ^{1}H NMR (500 MHz, DMSO) δ 8.49-7.15 (14H), 4.90-4.12 (4H), 3.31-2.61 (4H). ^{13}C NMR (126 MHz, DMSO) δ 137.9, 133.6, 132.4, 129.2, 128.9, 127.1, 126.1, 122.4, 51.2, 36.0.

P9(AK1/AZ5/Se) light yellow soild, 62.4mg, yield: 81%, M_n = 11,900 g/mol, M_w = 18,500 g/mol, M_w /M_n = 1.55. ^{1}H NMR (500 MHz, DMSO) δ 7.93-7.63 (12H), 4.56-4.24 (4H), 3.72-3.45 (4H), 1.97-1.40 (8H). ^{13}C NMR (101 MHz, DMSO) δ 168.5, 134.8, 133.4, 132.6, 132.1, 128.2, 125.8, 123.5, 49.7, 37.2, 27.5, 25.5.

P10(AK6/AZ6/Se) light yellow soild, 49.2mg, yield: 88%, M_n = 8,400 g/mol, M_w = 11,200 g/mol, M_w /M_n = 1.32. ^{1}H NMR (500 MHz, DMSO) δ 7.79-7.31 (10H), 5.83-4.98 (4H). ^{13}C NMR (126 MHz, DMSO) δ 143.7, 135.7, 131.9, 130.1, 128.7, 127.4, 124.2, 121.7, 52.5.

P11(AK7/AZ6/Se) light yellow soild, 54.4mg, yield: 85%, M_n = 7,900 g/mol, M_w = 9,000 g/mol, M_w /M_n = 1.14. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.39-7.00 (14H), 5.76-5.21 (4H), 4.28-3.96 (4H). ^{13}C NMR (126 MHz, DMSO) δ 135.2, 132.9, 129.9, 129.5, 128.8, 128.3, 127.7, 126.9, 52.4, 28.7.

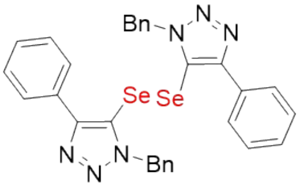
7. Low copper catalyst loading

In a 2 ml glass vial, **CuI** (0.001 mmol, 0.18 mg, 1 mol%), **Me$_4$phen** (0.0012 mmol, 0.3mg, 1.2 mol%), were dissolved in $CHCl_3/H_2O$ (v/v=1/1, 1.0 ml), stirring for 5-10 min. **TBAB** (0.1 mmol, 32.2 mg, 1 equiv), **AK1** (0.1 mmol, 12.6 mg, 1 equiv.) **AZ1** (0.6 mmol, 80.4 mg, 6 equiv.) **Se** (1.2 mmol, 95 mg, 12 equiv.) and **CS_2CO_3** (0.6 mmol, 195.6 mg, 6 equiv) was then added. The mixture was stirred at 50℃ temperature for 12 h. The mixture was filtered through a microfiltration membrane. The filtrate was precipitated with 20 mL methanol. The products were washed with methanol for three times and collected by centrifugation. The polymer P1-low was dried in vacuo and characterized by GPC.

P1-Low (AK1/AZ1/Se) light yellow soild, 28.1 mg, yield: 51%, Mn = 21,300 g/mol, Mw = 25,900 g/mol, Mw /Mn = 1.21. Experimentally, it was demonstrated that 1% copper was still able to catalyse the polymerisation, with a slight decrease in yield for the same amount of time.

8. Preparation of the small molecule template compound M1

In a 2 ml glass vial, **CuI** (0.005 mmol, 0.9 mg, 5 mol%), **Me$_4$phen** (0.006 mmol, 1.5mg, 6 mol%), were dissolved in $CHCl_3/H_2O$ (v/v=1/1, 1.0 ml), stirring for 5-10 min. **TBAB** (0.1 mmol, 32.2 mg, 1 equiv), **phenylacetylene**(0.1 mmol, 10.2 mg, 1 equiv.) **(Azidomethyl)benzene** (0.3 mmol, 39.9 mg, 3equiv.) **Se** (0.6 mmol, 47.5 mg, 6equiv.) and **CS_2CO_3** (0.3 mmol, 97.8 mg, 3equiv) was then added. The mixture was stirred at 50℃ temperature for 12 h. **M1** light yellow soild, 47.7 mg, yield: 76%



M1

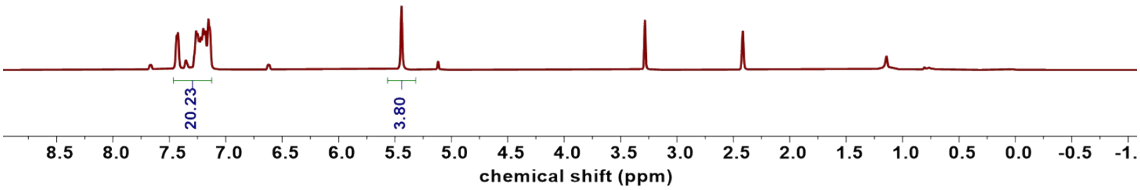


Figure S1 ^{1}H NMR spectrum of M1

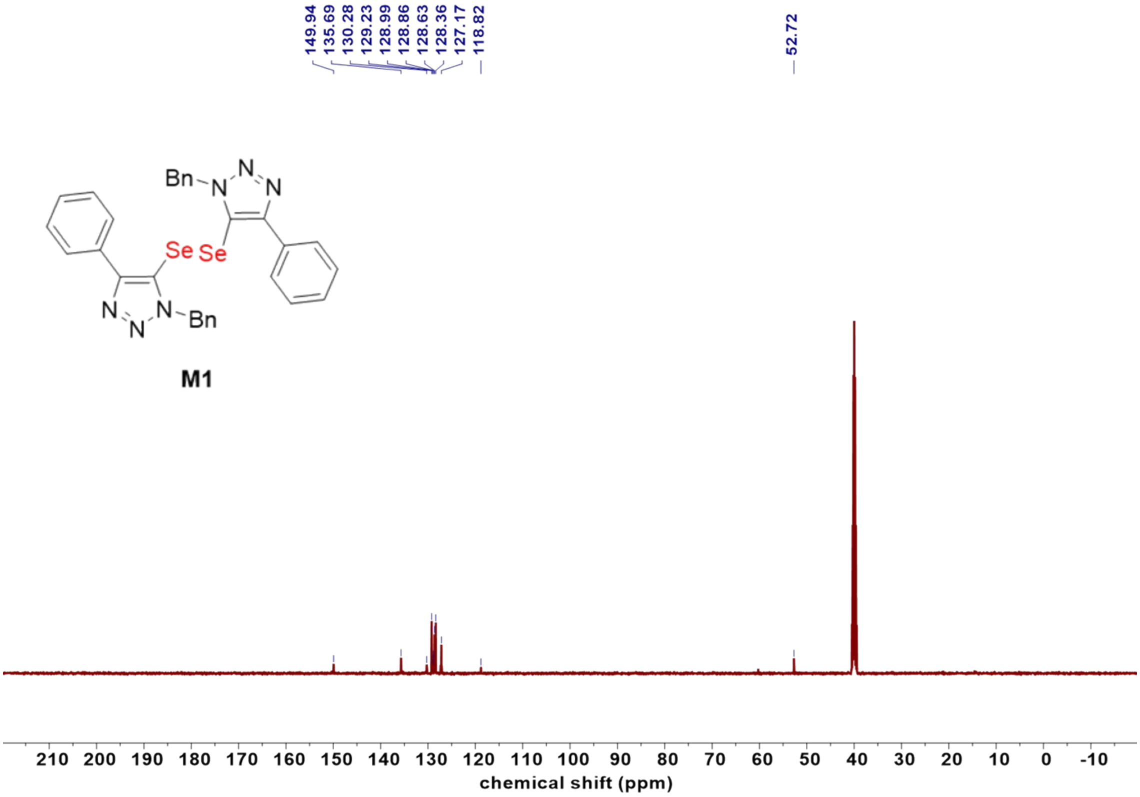


Figure S2 ^{13}C NMR spectrum of M1

9. Degradable polymers responsive to H_2O_2 or DTT.

Polymer P1 (10.0 mg) was weighed and dissolved in 1 mL of H_2O_2/DMF (5 mmol/L) and DTT/DMF (5 mmol/L), and the reaction was stirred at 37 °C, and the polymers were sampled at different reaction times. The molecular weight of the polymer was then determined by GPC. The degradation products were characterized by HR-MS.

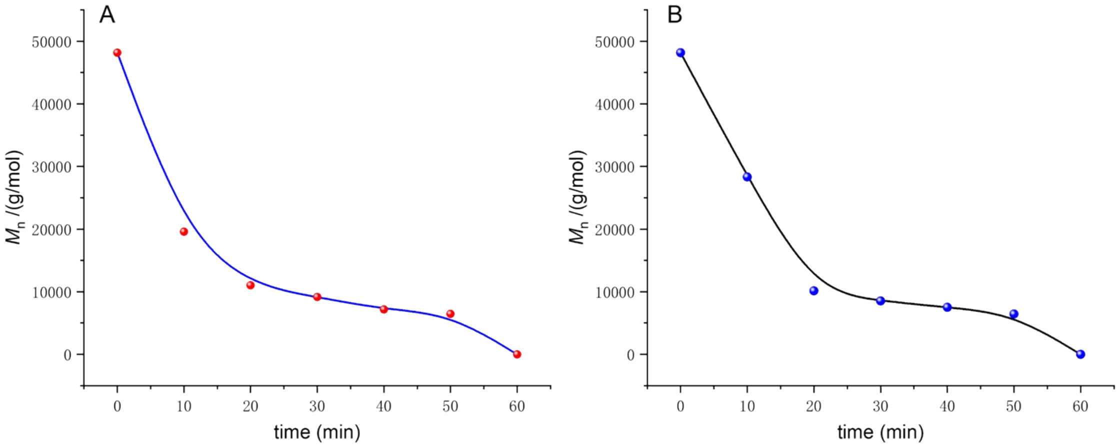


Figure S3 Polymer degradation curve in H_2O_2 (A) and DTT (B).

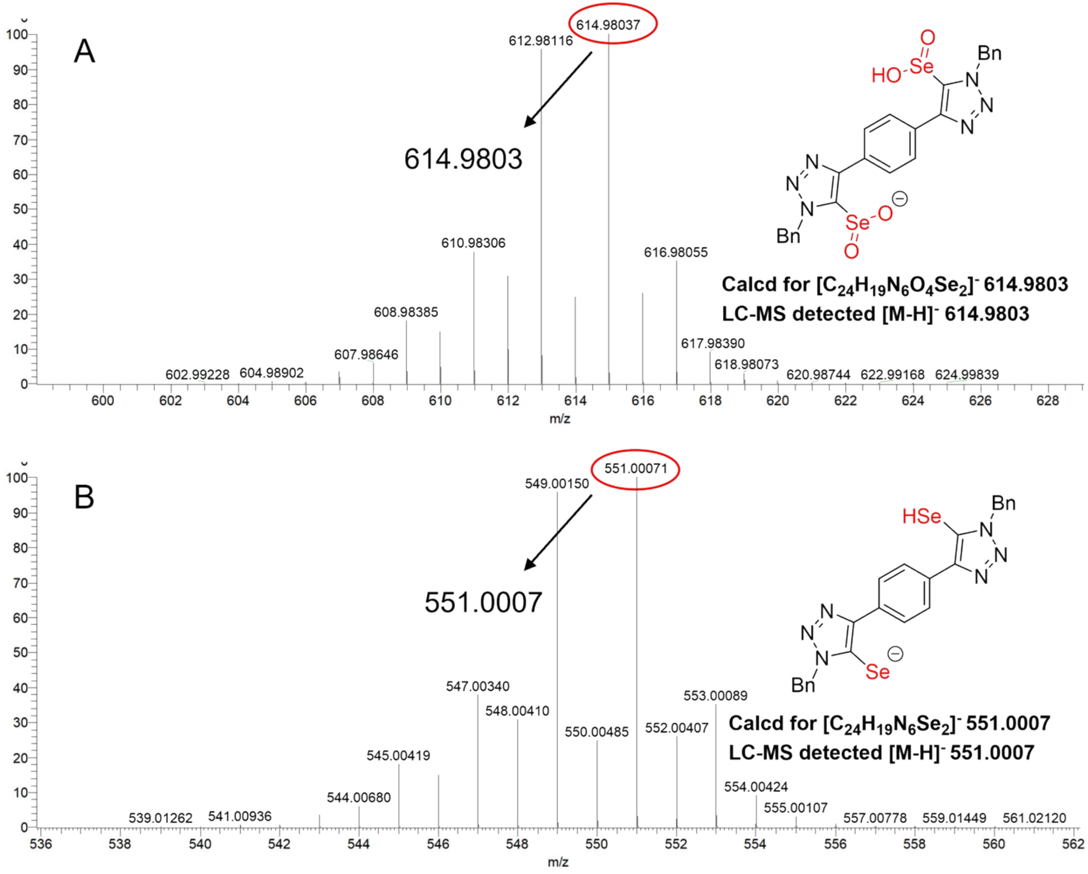


Figure S4 HR-MS of Polymer degradation products are in H_2O_2 (A) or DTT (B).

The degraded polymers were extracted by gradient extraction with EA and water and concentrated by reduced pressure rotary evaporation before the degradation products were analysed for their chemical state by X-ray photoelectron spectroscopy (XPS). The characterisation results showed that the Se3d orbital binding energy of the H_2O_2-treated samples was higher than that of the DTT-treated group, and the difference in this value was highly consistent with the law that the characteristic binding energy of selenate is higher than that of selenol in the XPS standard manual. The differential bond-breaking degradation of the dynamic diselenide bonds in the polymer under oxidising/reducing conditions was confirmed.

Analysis of the chemical groups in the degradation products by infrared spectroscopy (IR) revealed distinct absorption bands: stretching vibrations of the -C-Se bond at 616 cm^{-1} (P1-H_2O_2) and 615 cm^{-1}(P1-DTT), and stretching vibrations of the -Se-H bond at 3360 cm^{-1} (P1-H_2O_2) and 3304 cm^{-1} (P1-DTT). Additionally, a stretching vibration peak corresponding to the Se=O bond in selenious acid (-SeO_2) was observed at 882 cm^{-1} in the oxidized product P1-H_2O_2. The FTIR results demonstrate that diselenide bonds undergo cleavage under oxidizing conditions to form selenious acid derivatives, whereas reducing conditions promote degradation into selenol (-SeH) structures.

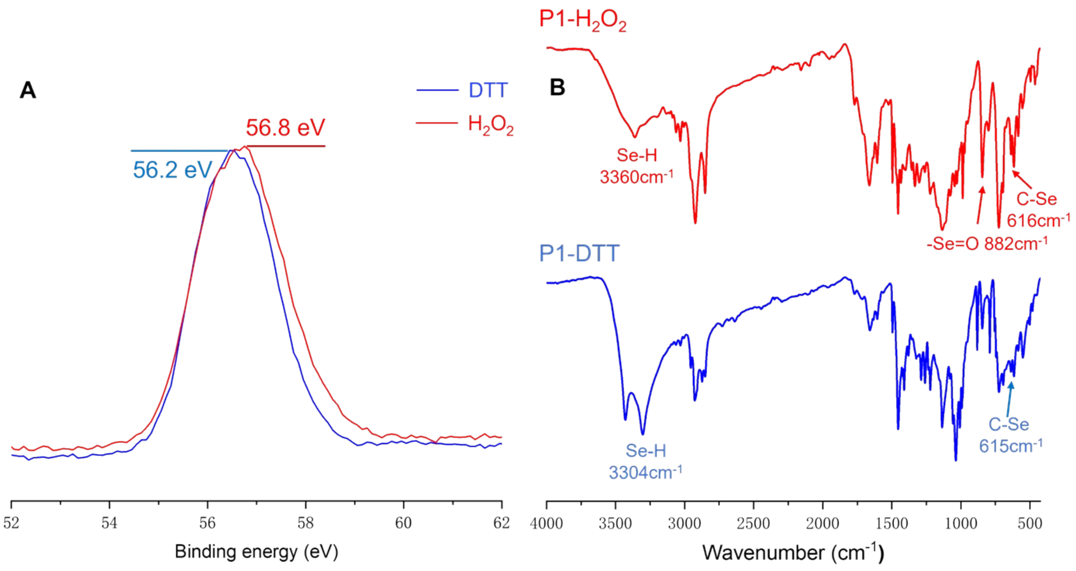


Figure S5 XPS and FT-IR of Polymer degradation products are in H_2O_2 or DTT.

10. Proposed mechanism.

A possible mechanism for this MCP was proposed in Scheme 4 basing on mechanistic studies and literatures report.[3] Initially, Se^{2-} and SeO_3^{2-} species were generated through disproportionation of elemental selenium in the presence of base (Cs_2CO_3). Se^{2-} further reacted with elemental selenium to produce key intermediate Se_2^{2-}.

Meanwhile, the monomer diyne AK1 could be converted to cuprous di-acetylide intermediate A using copper as catalyst, which then underwent cycloaddition reaction with azide AZ1 to form 5-cuprated di-triazole intermediate B. Subsequently, a very special oxidative addition occurred from 5-cuprated di-triazole B with Se_2^{2-} by SeO_3^{2-} to afford Cu(III) intermediate C, which also determined the excellent regioselectivity for preparing 5-functionalized triazole. Finally, intermediate C underwent reductive elimination to provide diselenium polymer P1 with recovery of copper(I) catalyst.

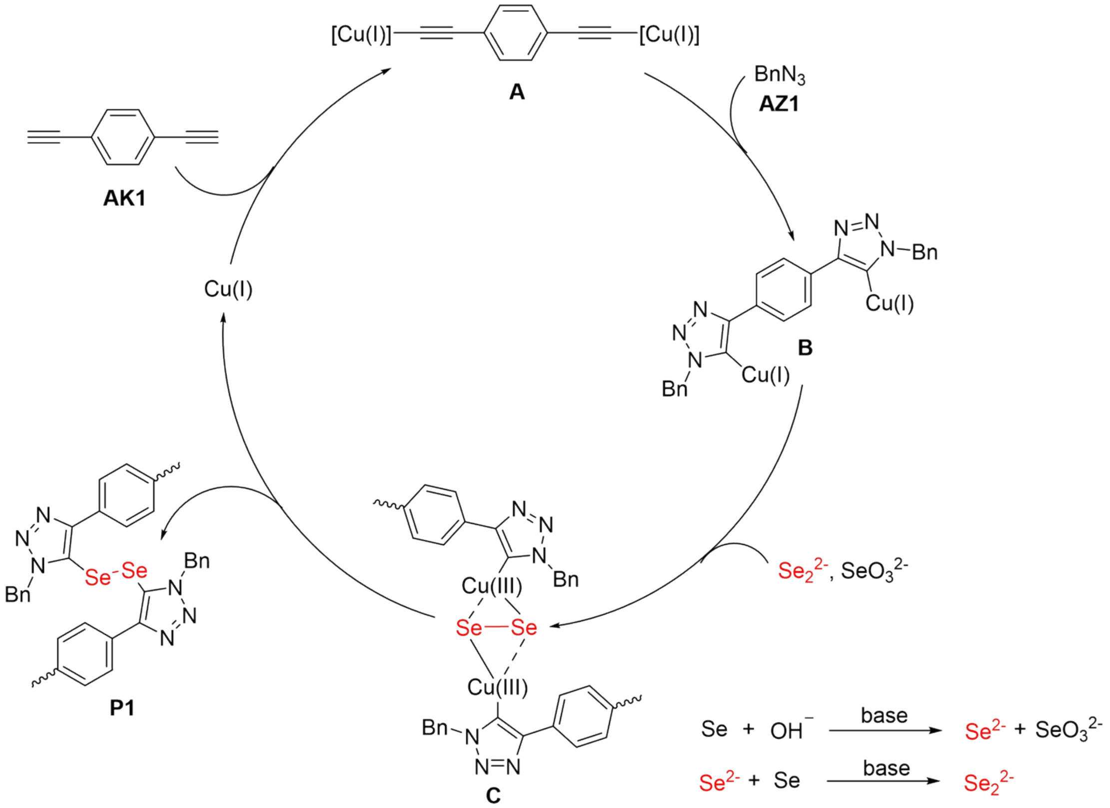


Figure S6 Proposed mechanism for the synthesis of poly(5-diselenide-triazole)s by MCP.

11. NMR spectra.

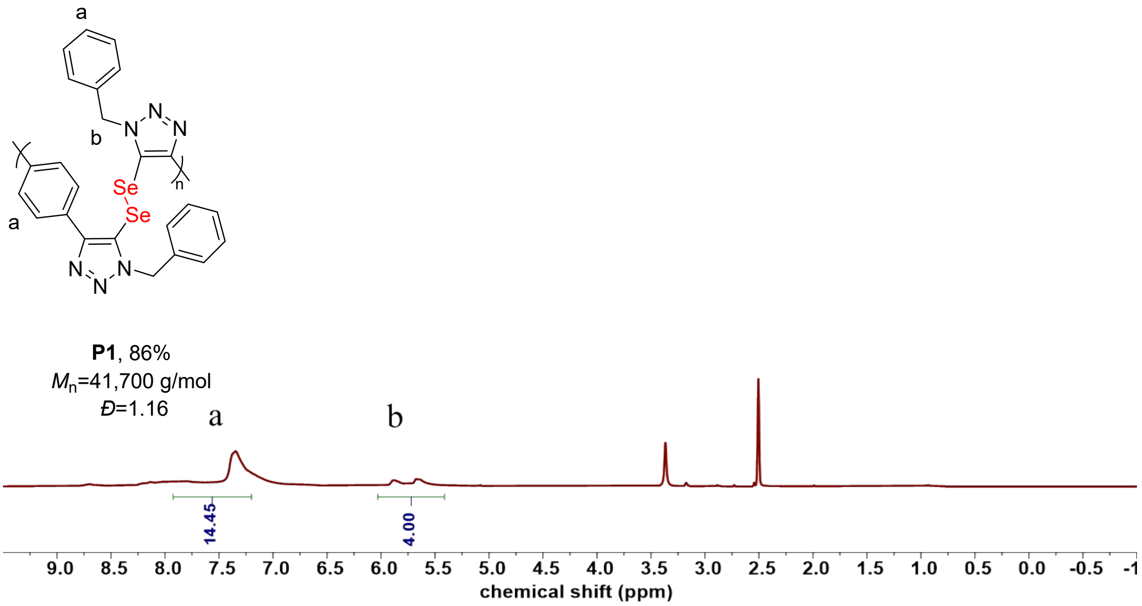


Figure S7 ^{1}H NMR spectrum of P1(AK1/AZ1/Se)

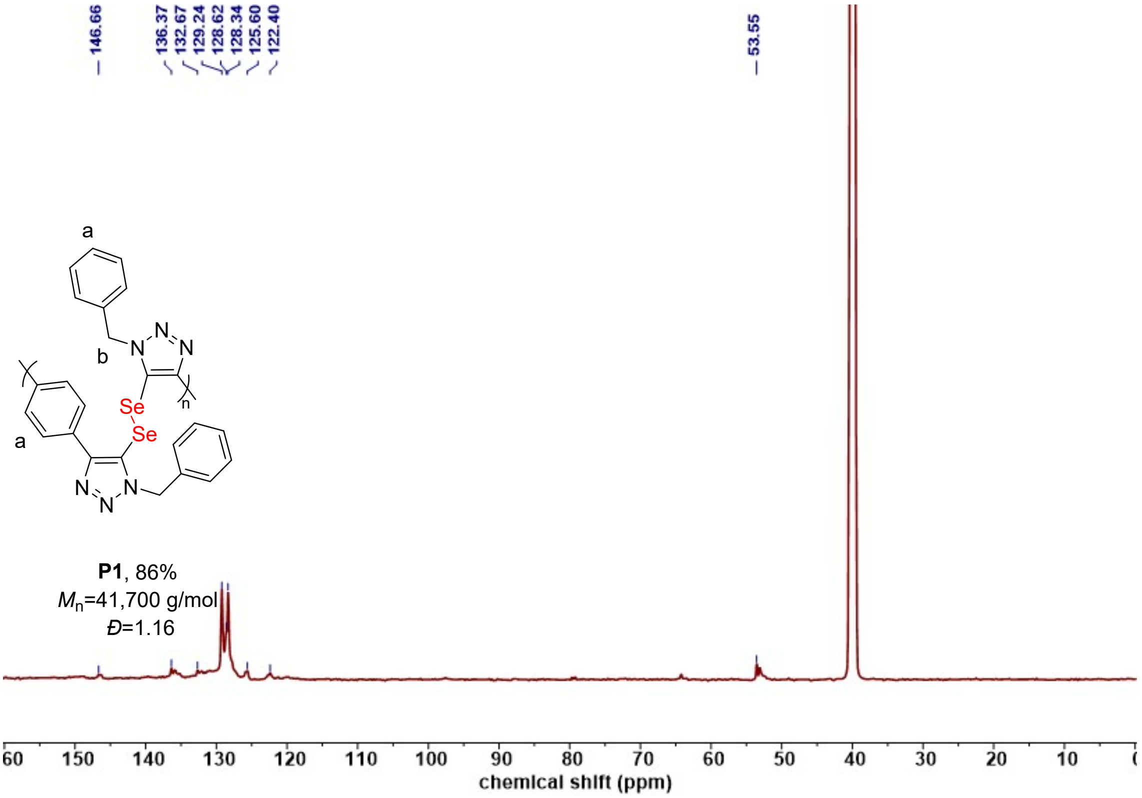


Figure S8 ^{13}C NMR spectrum of P1(AK1/AZ1/Se)

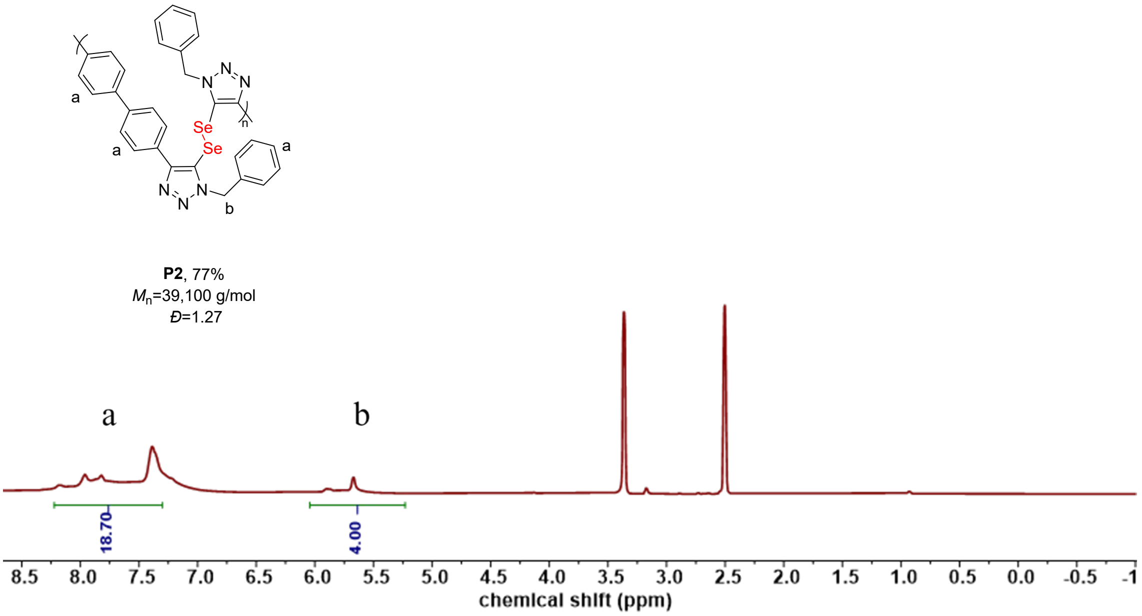


Figure S9 ^{1}H NMR spectrum of P2(AK2/AZ1/Se)

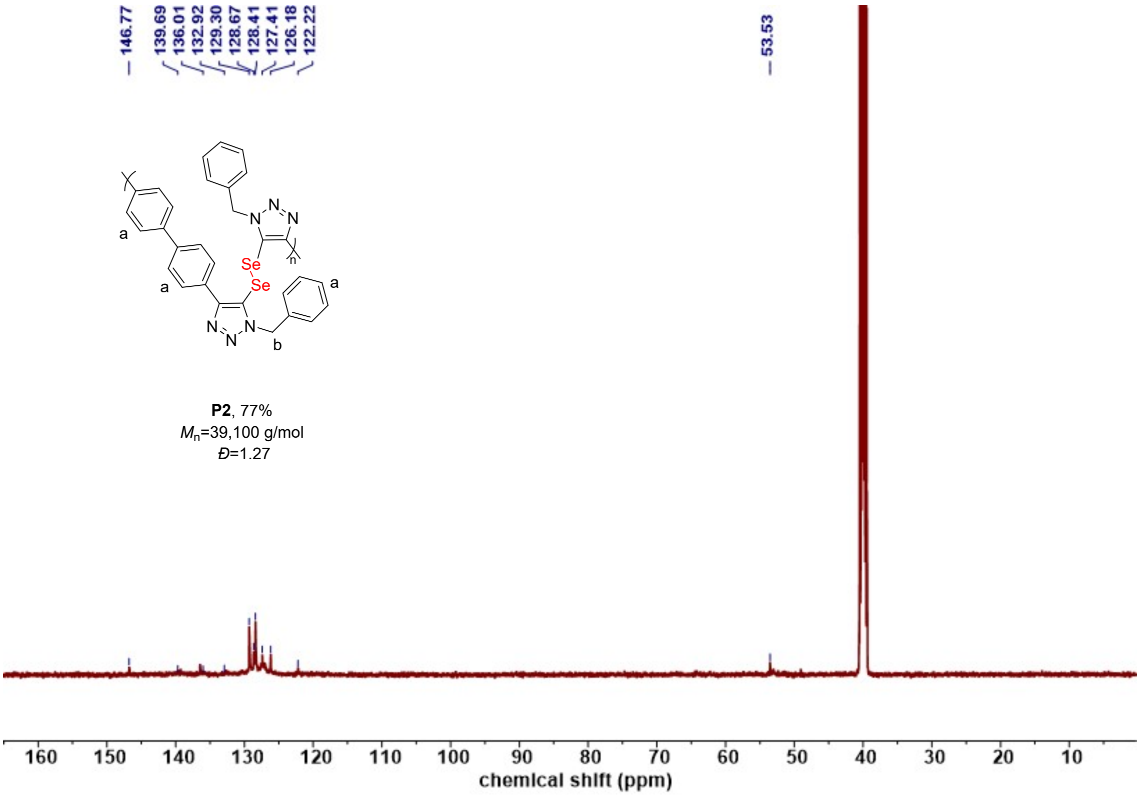


Figure S10 ^{13}C NMR spectrum of P2(AK2/AZ1/Se)

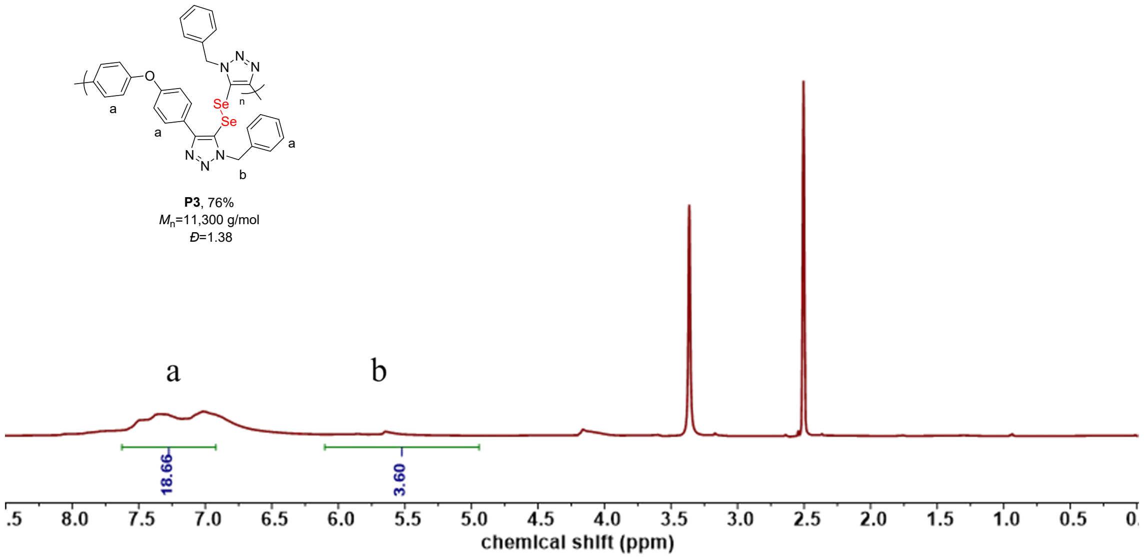


Figure S11 ^{1}H NMR spectrum of P3(AK3/AZ1/Se)

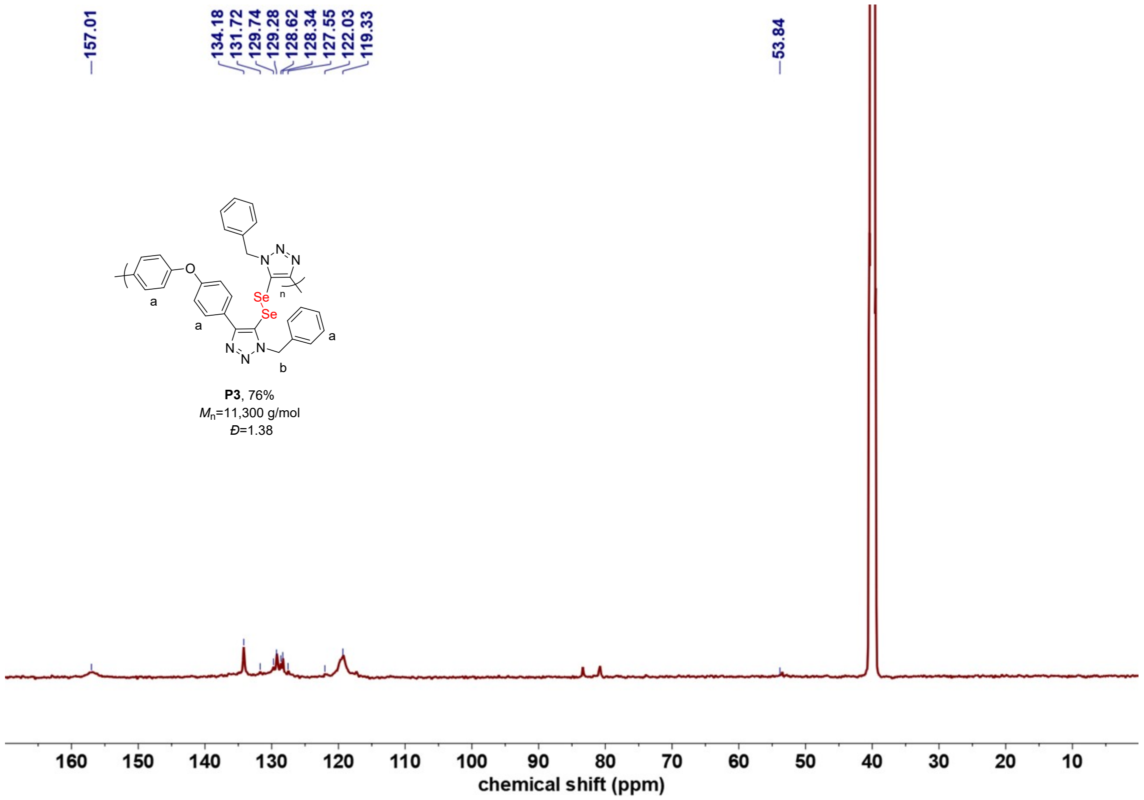


Figure S12 ^{13}C NMR spectrum of P3(AK3/AZ1/Se)

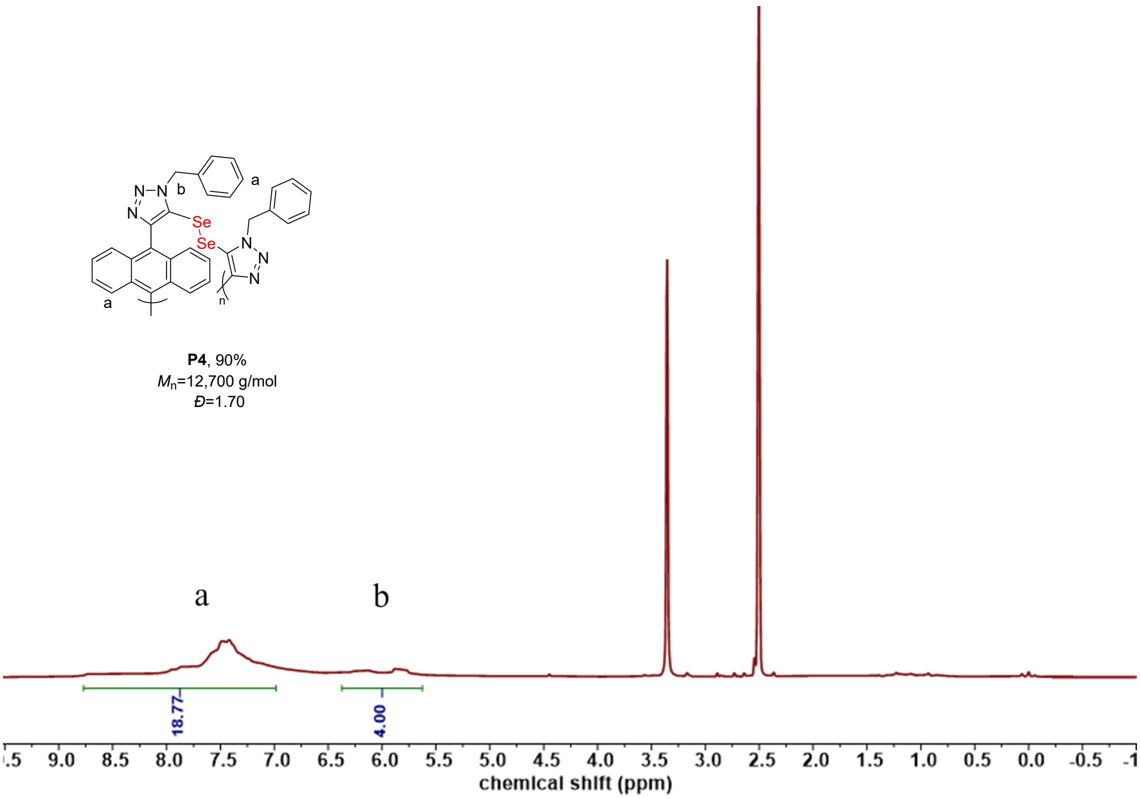


Figure S13 ^{1}H NMR spectrum of P4(AK4/AZ1/Se)

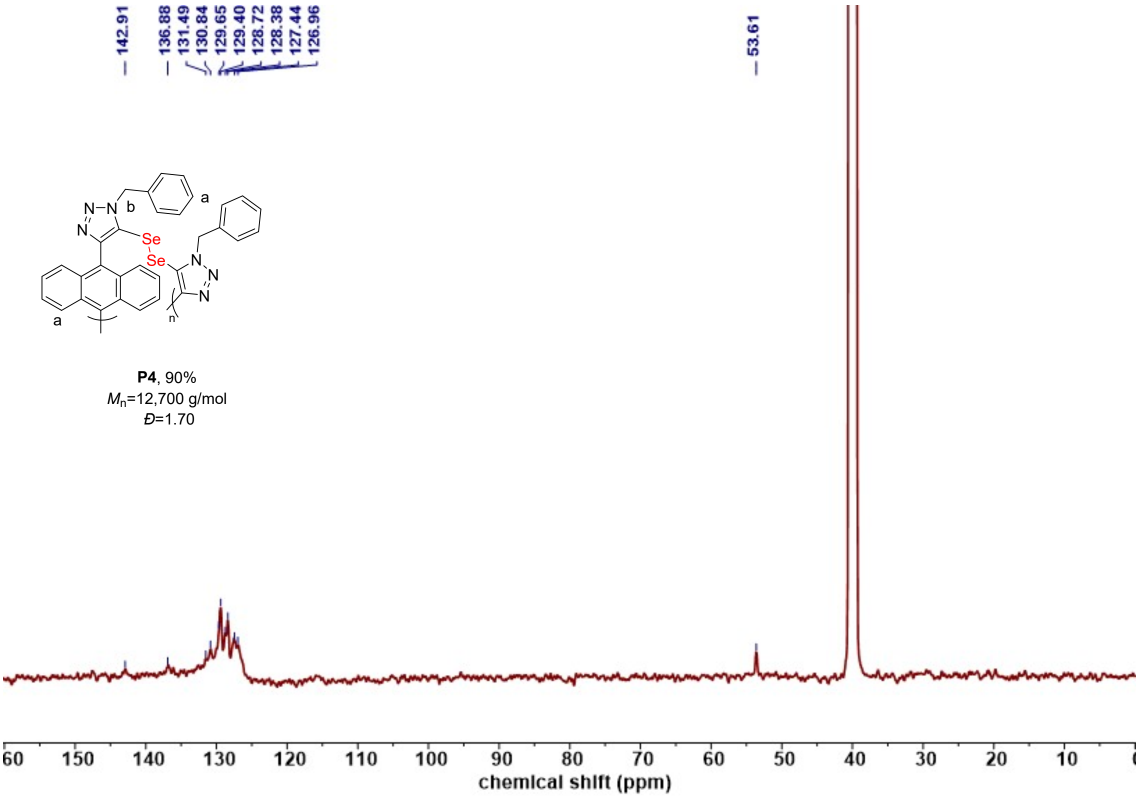


Figure S14 ^{13}C NMR spectrum of P4(AK4/AZ1/Se)

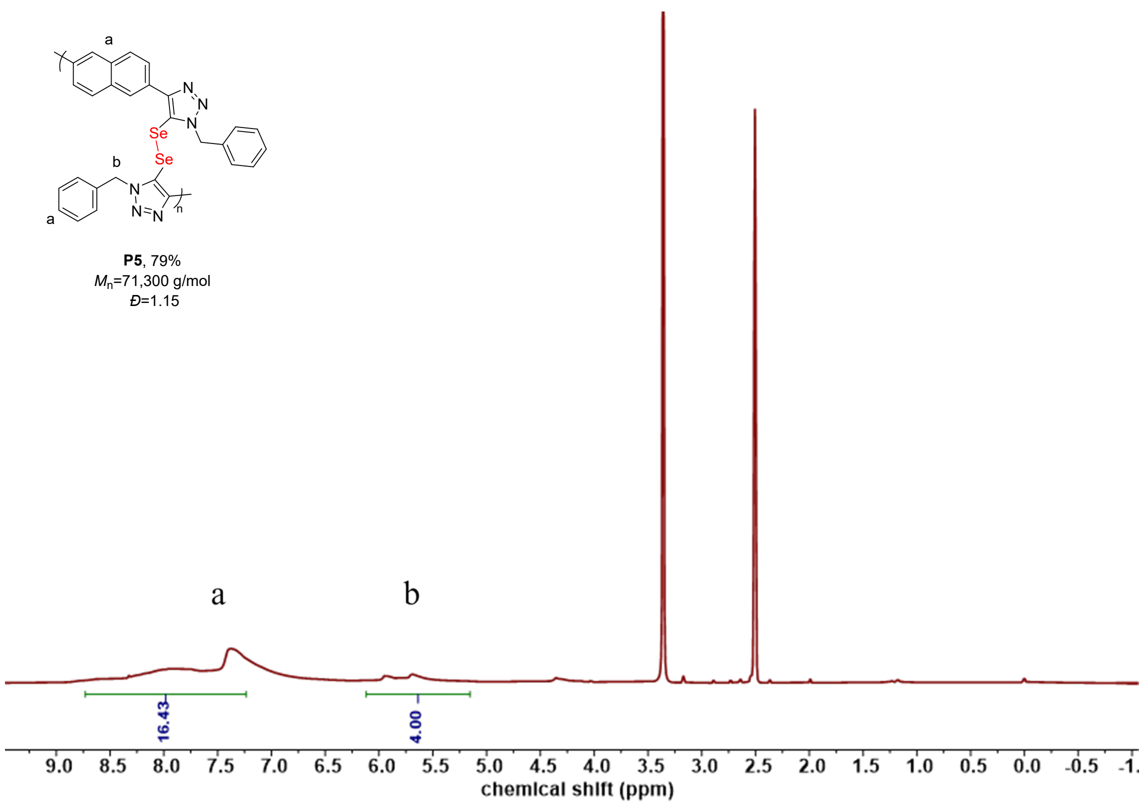


Figure S15 ^1H NMR spectrum of P5(AK5/AZ1/Se)

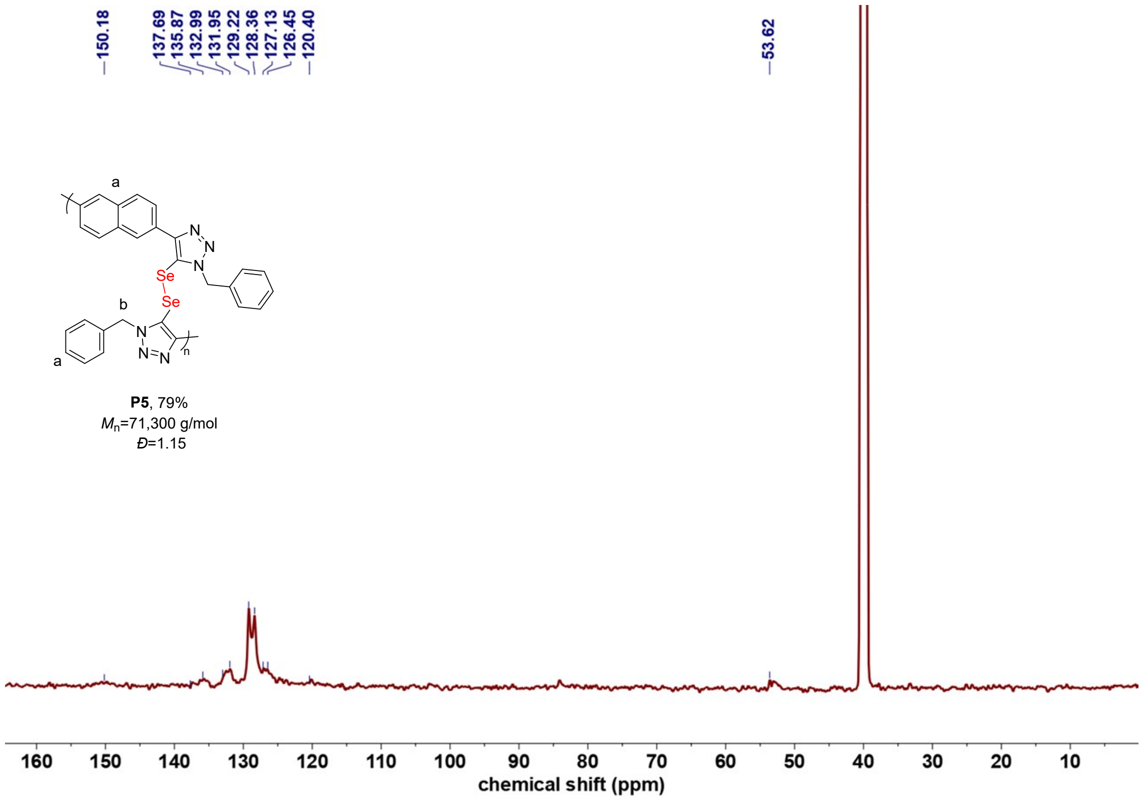


Figure S16 ^{13}C NMR spectrum of P5(AK5/AZ1/Se)

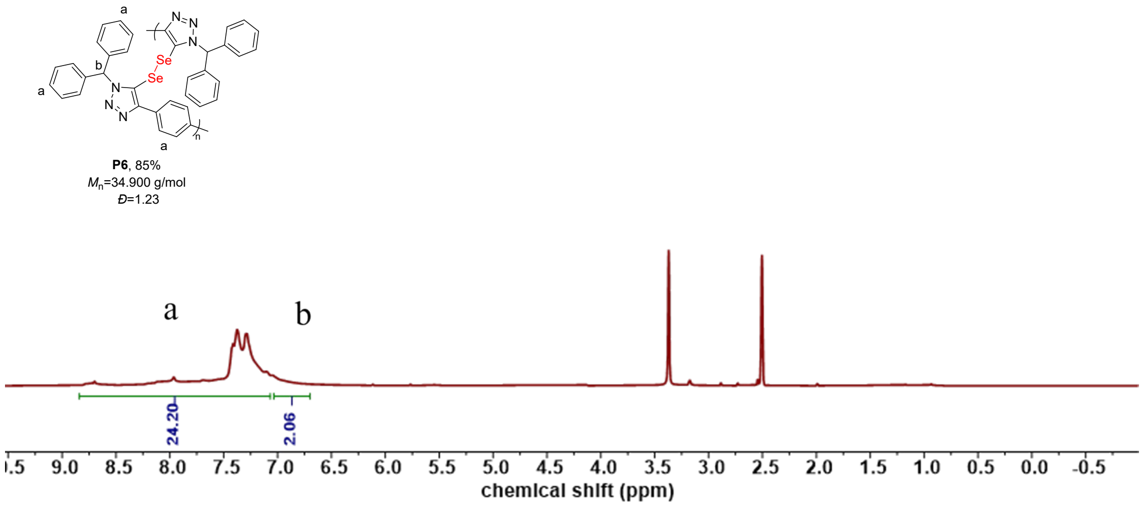


Figure S17 ^{1}H NMR spectrum of P6(AK1/AZ2/Se)

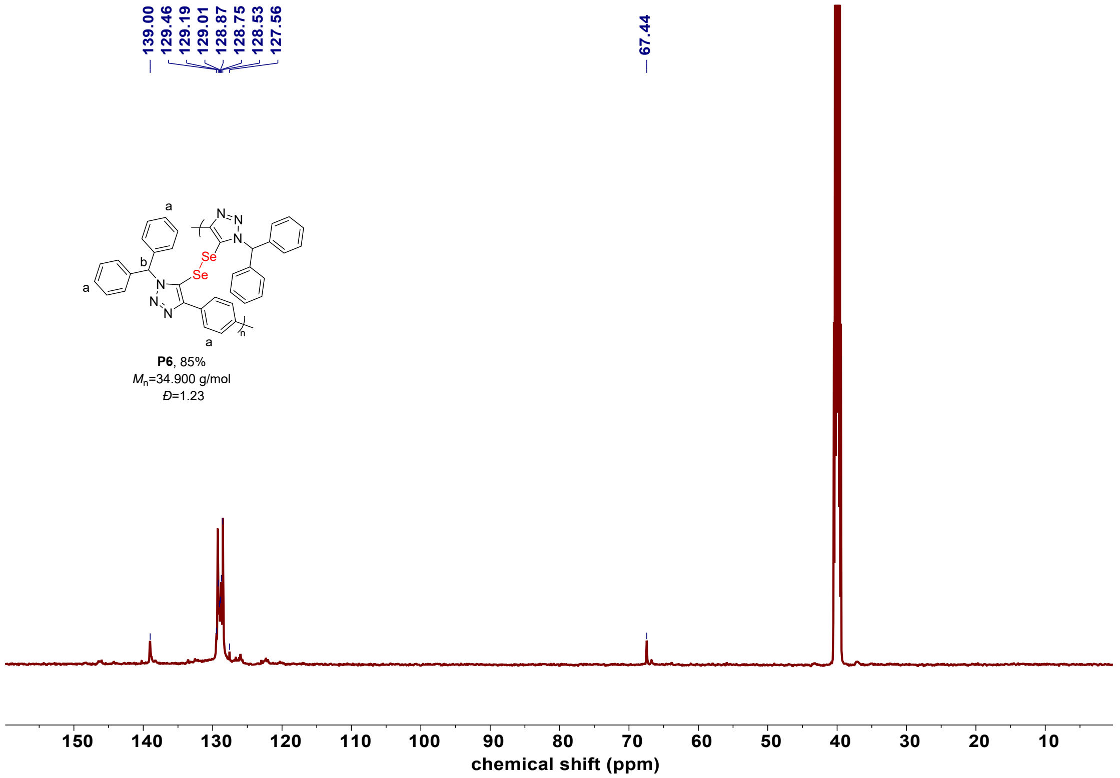


Figure S18 ^{13}C NMR spectrum of P6(AK1/AZ2/Se)

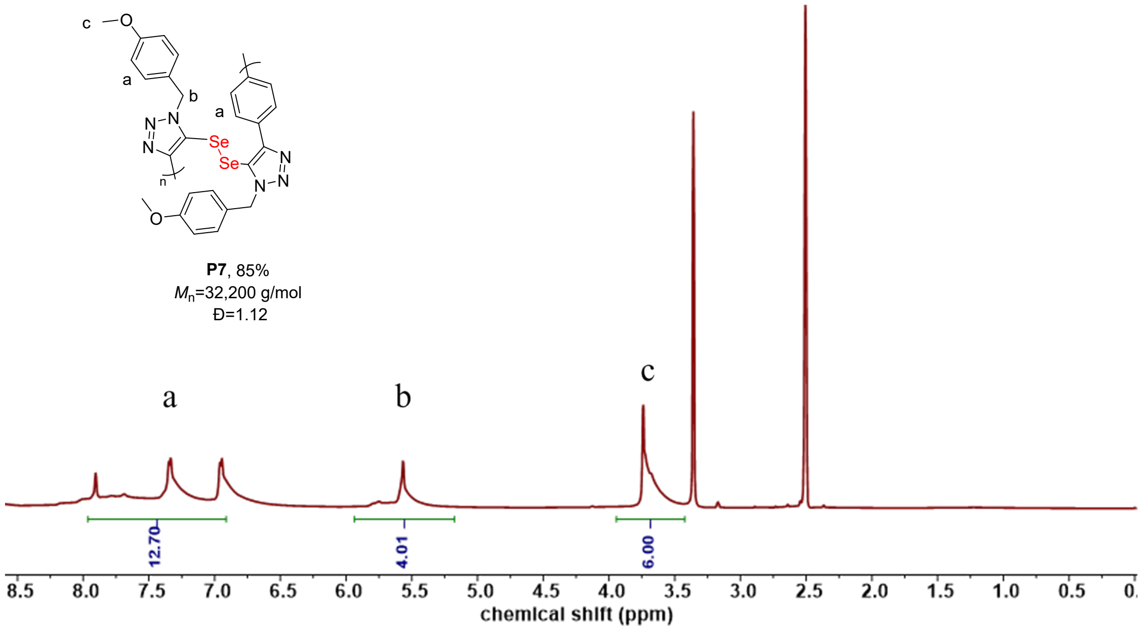


Figure S19 ^{1}H NMR spectrum of P7(AK1/AZ3/Se)

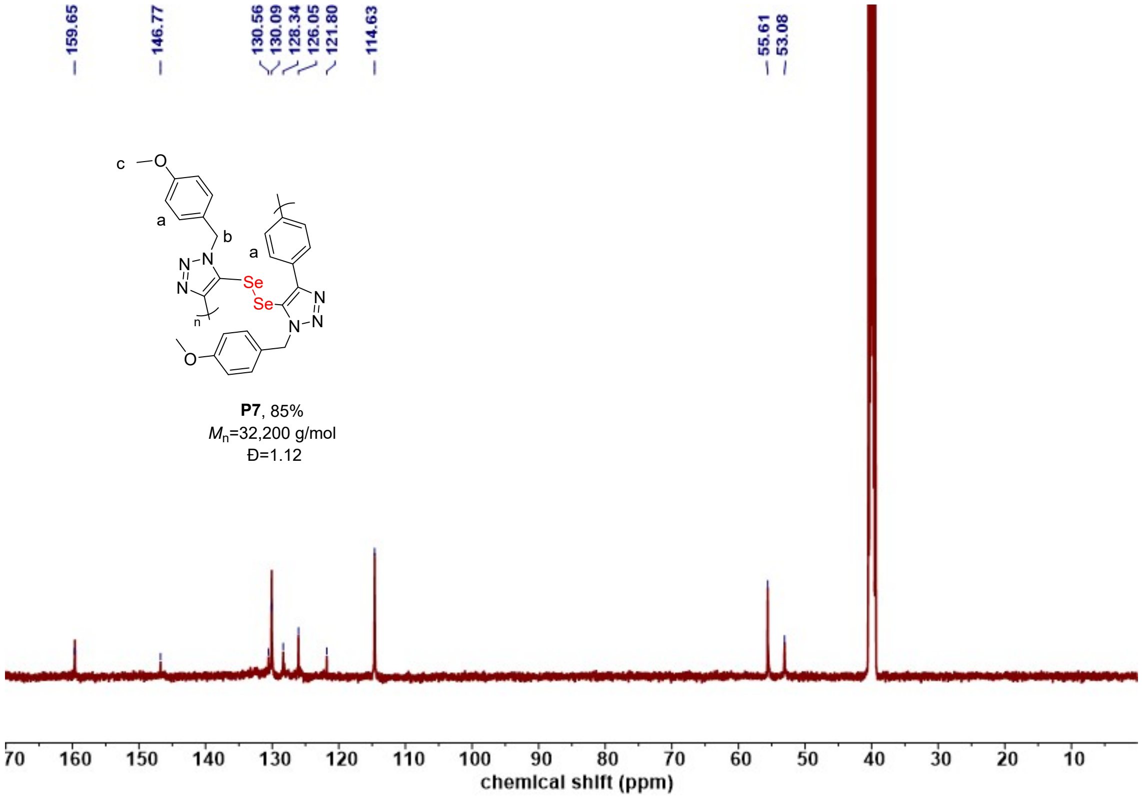


Figure S20 ^{13}C NMR spectrum of P7(AK1/AZ3/Se)

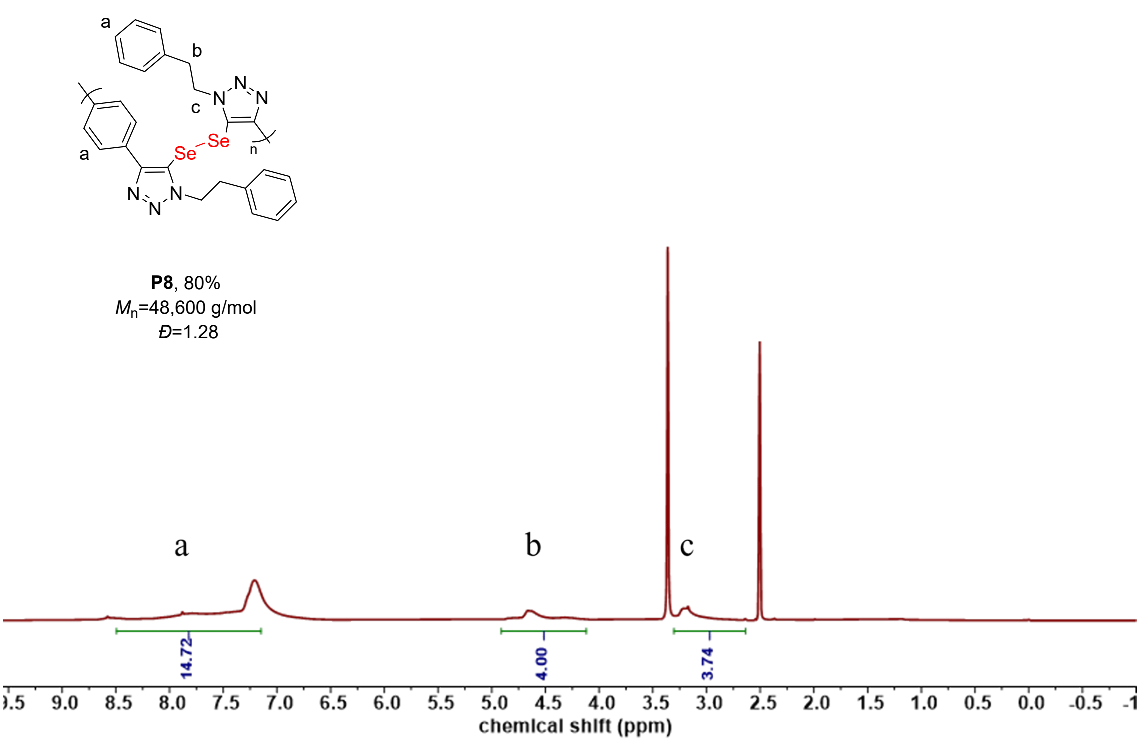


Figure S21 ^{1}H NMR spectrum of P8(AK1/AZ4/Se)

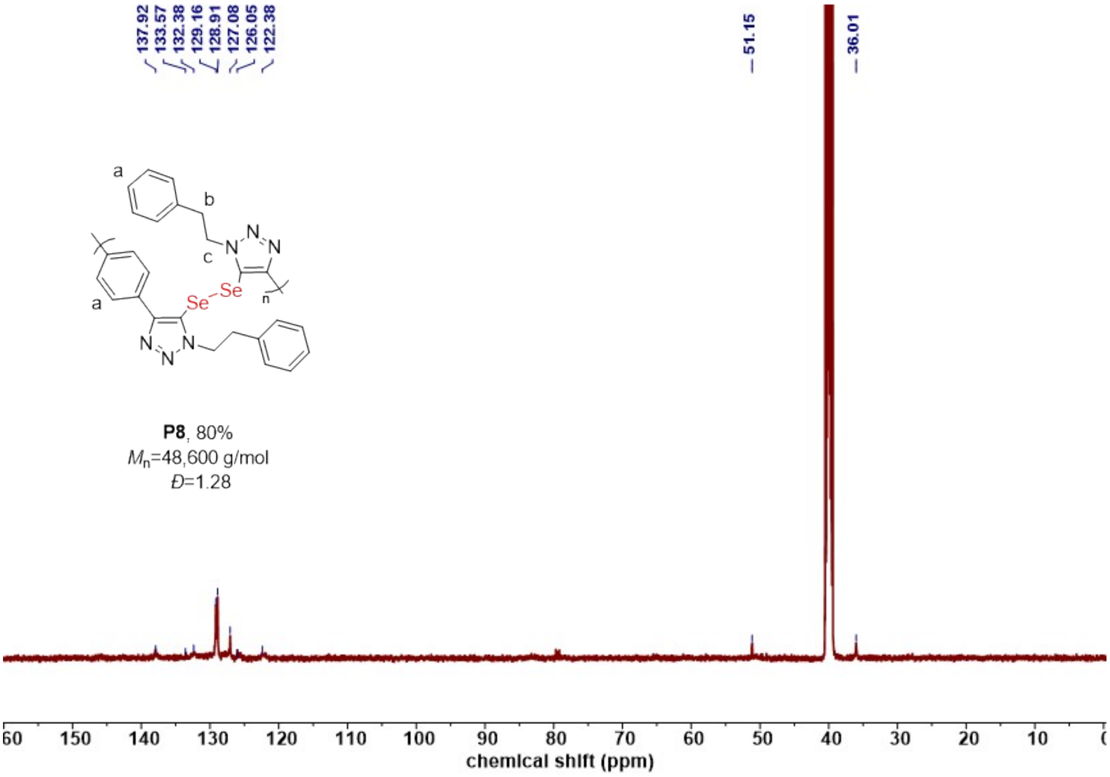


Figure S22 ^{13}C NMR spectrum of P8(AK1/AZ4/Se)

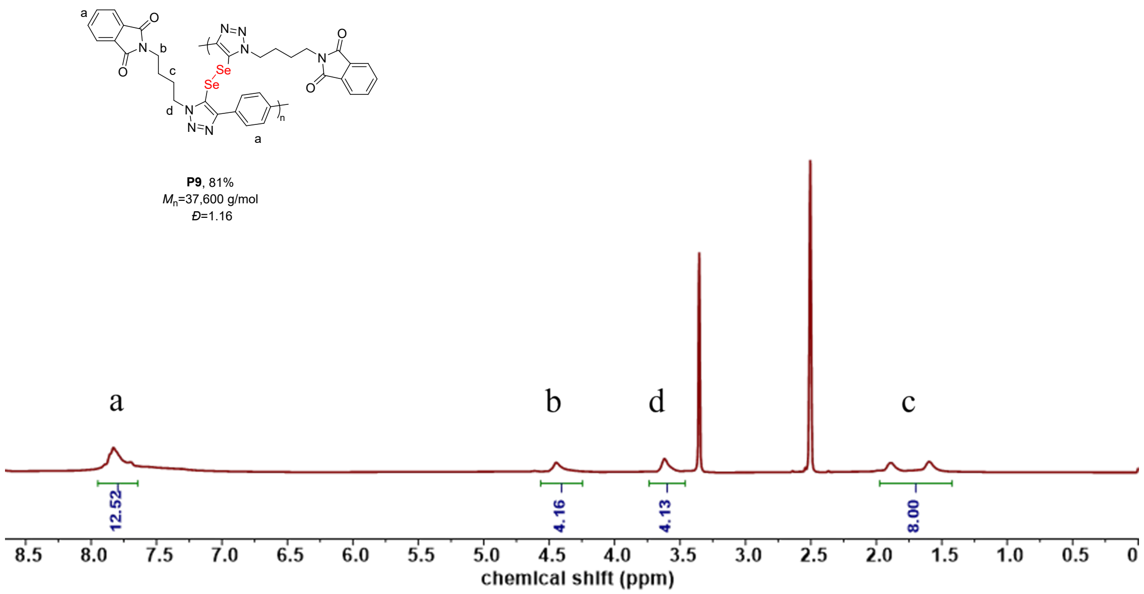


Figure S23 ^{1}H NMR spectrum of P9(AK1/AZ5/Se)

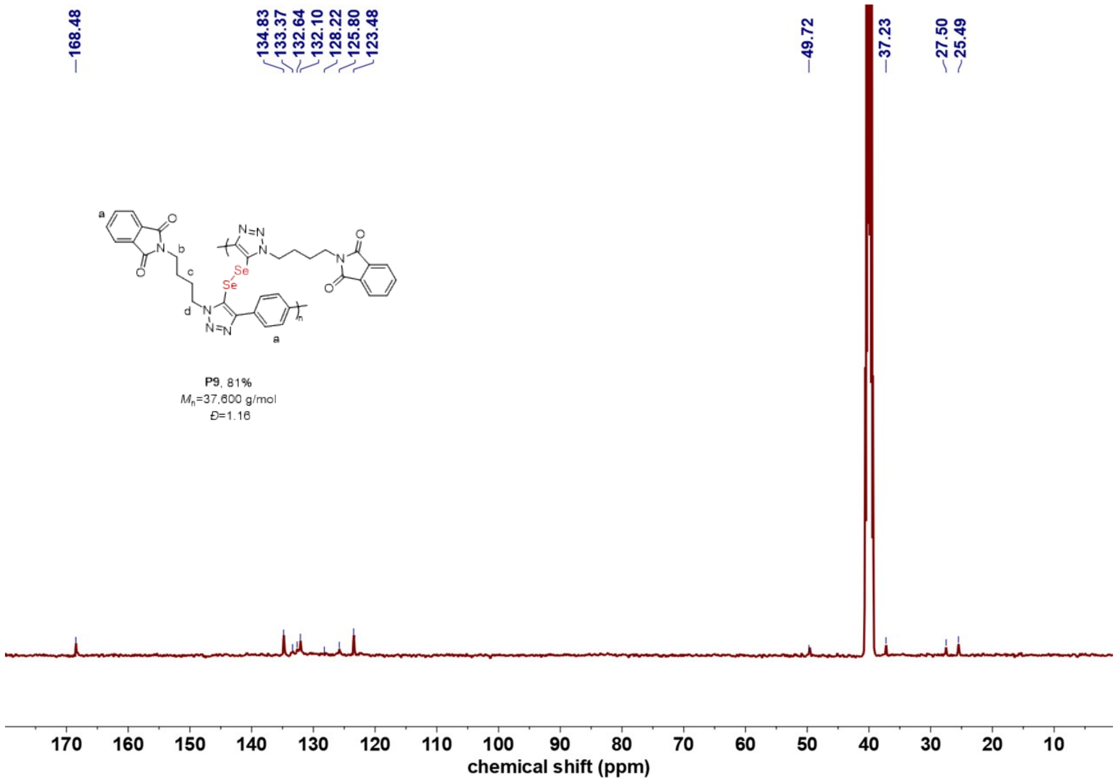


Figure S24 ^{13}C NMR spectrum of P9(AK1/AZ5/Se)

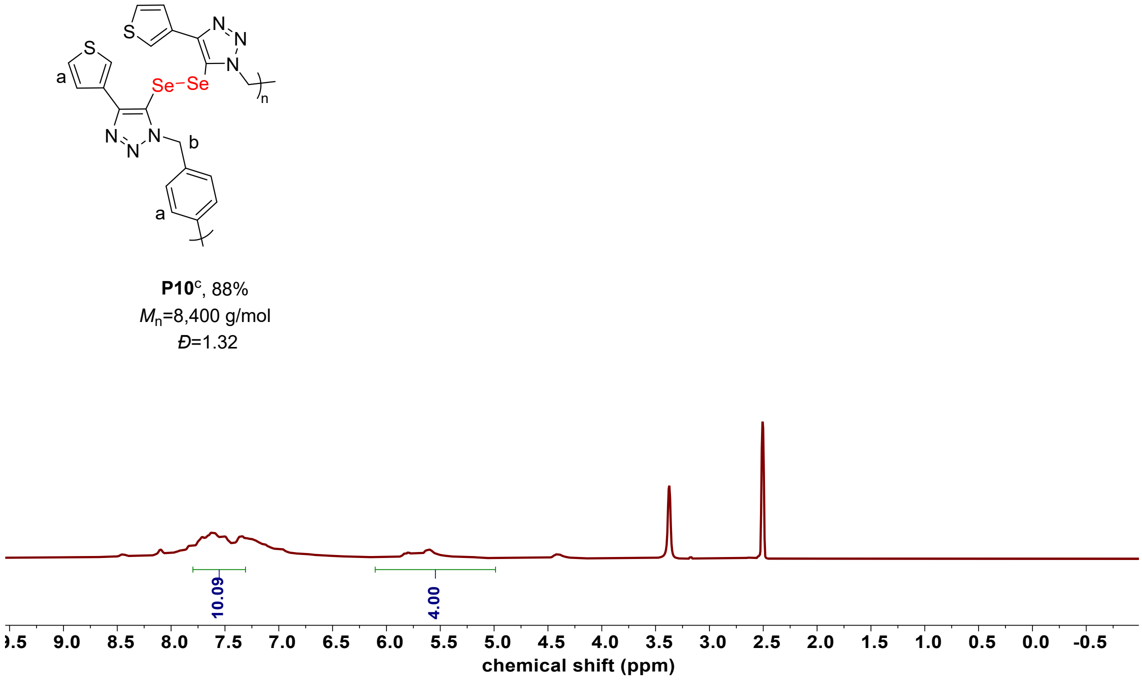


Figure S25 ^{1}H NMR spectrum of P10(AK6/AZ6/Se)

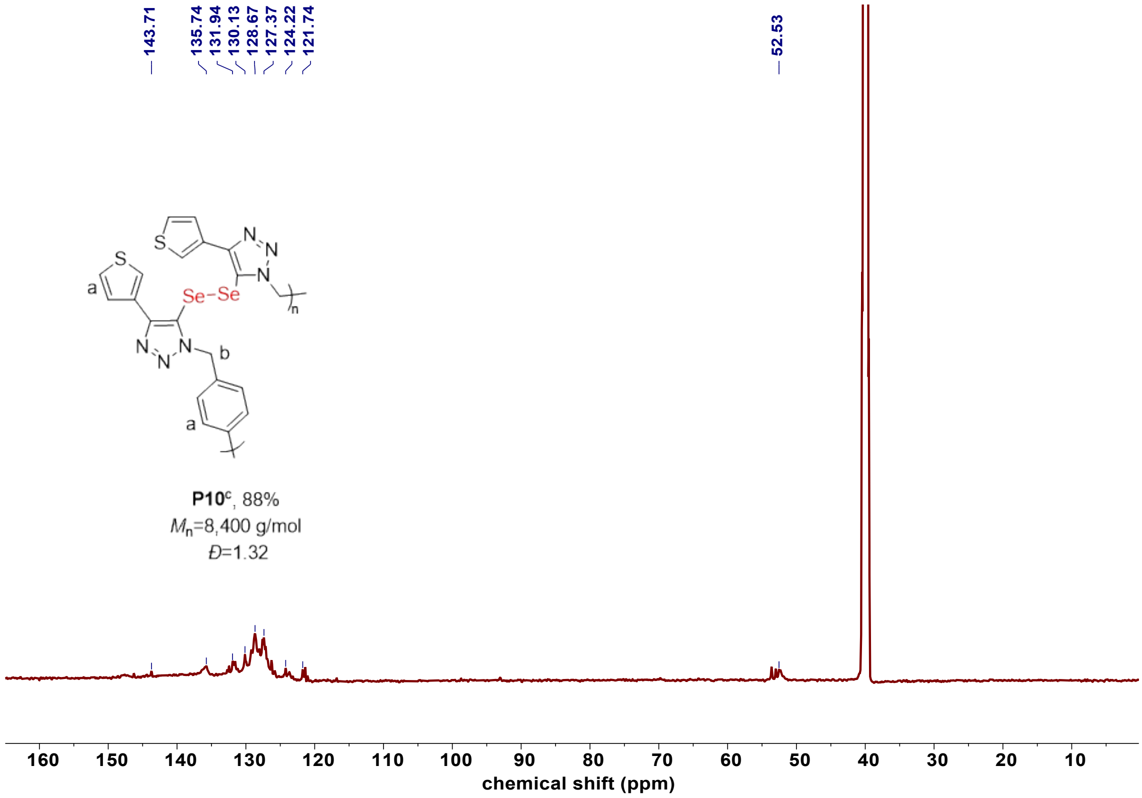


Figure S26 ^{13}C NMR spectrum of P10(AK6/AZ6/Se)

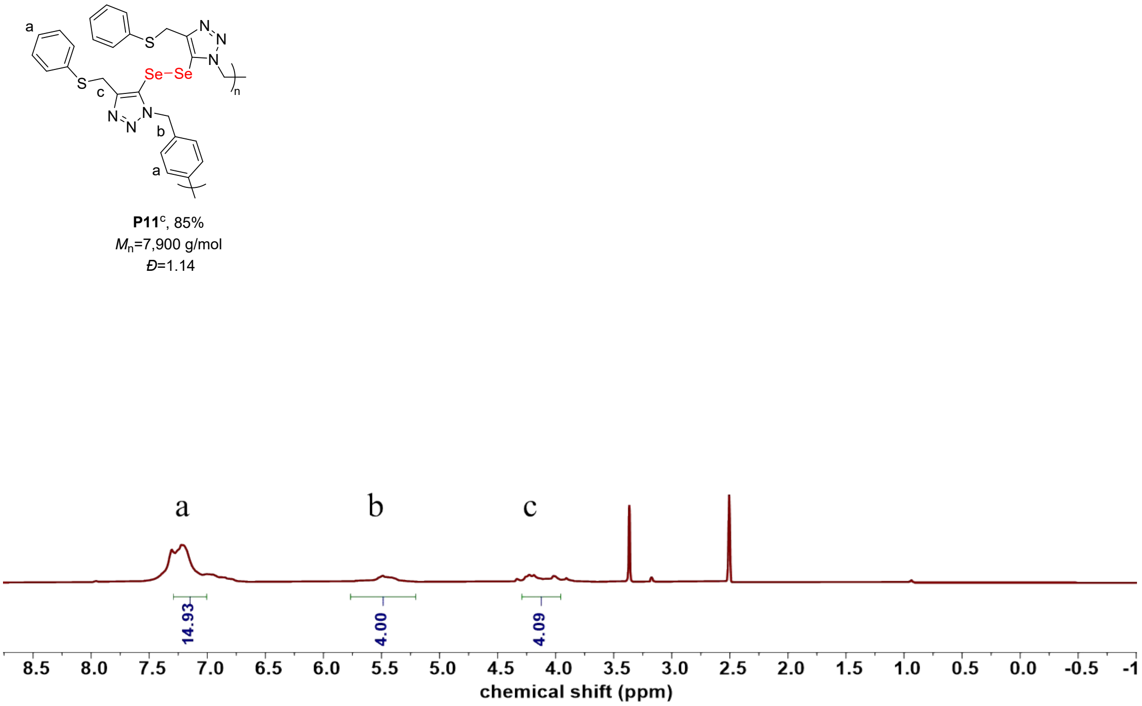


Figure S27 ^{1}H NMR spectrum of P11(AK7/AZ6/Se)

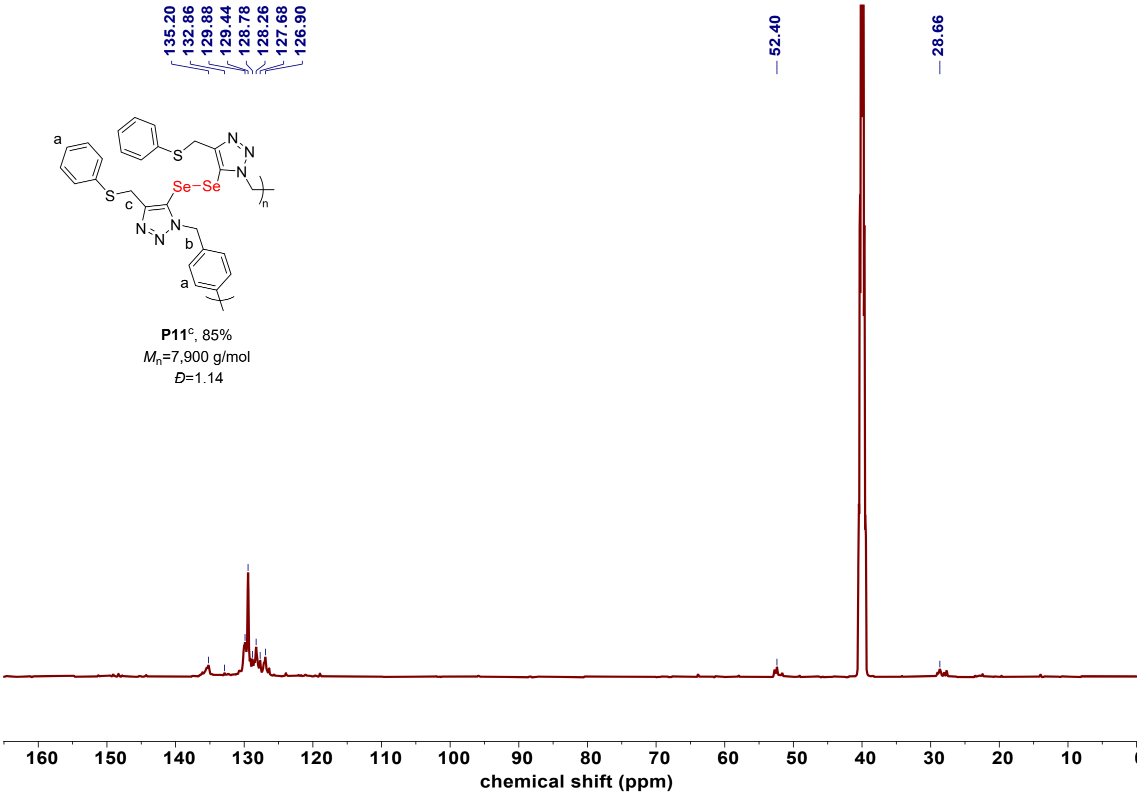


Figure S28 ^{13}C NMR spectrum of P11(AK7/AZ6/Se)

12. GPC traces of P1-P11.

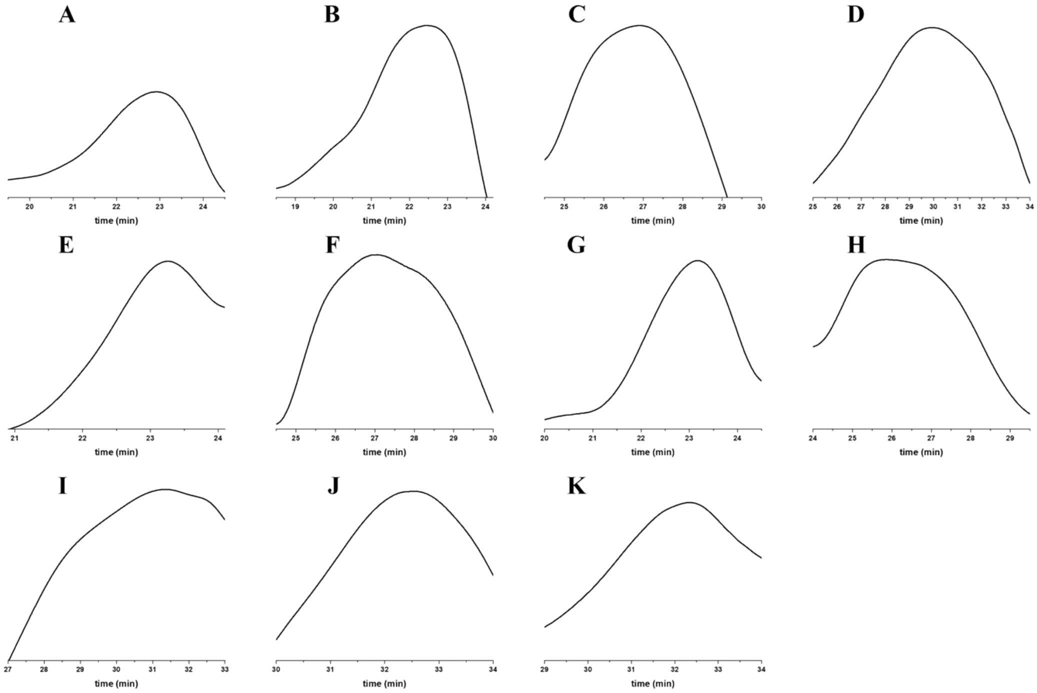


Figure S29. GPC traces of P1-P11. P1 (A, *Đ*=1.16), P2 (B, *Đ*=1.27), P3 (C, *Đ*=1.38), P4 (D, *Đ*=1.70), P5 (E, *Đ*=1.15), P6 (F, *Đ*=1.23), P7 (G, *Đ*=1.12), P8 (H, *Đ*=1.28), P9 (I, *Đ*=1.55), P10 (J, *Đ*=1.32), P11 (K, *Đ*=1.14). M_n, M_w and Đ were determined by GPC in DMF with PS (polystyrene) standards.

13. Kinetics of polymers.

The polymerization kinetics data were obtained through a standardized experimental procedure: After the reaction started, samples were taken at fixed time intervals. The AK1 conversion was quantitatively analyzed using proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, while the polymer molecular weight was determined by gel permeation chromatography (GPC) under identical conditions. Kinetic profiles of the polymerization process were subsequently constructed.

Specifically, the AK1 conversion was calculated based on the integration ratio between the characteristic proton signals in the ^{1}H NMR ($CHCl_3$) spectra: the terminal alkyne hydrogen (δ = 3.0 ppm) and the methylene hydrogen in benzyl azide (δ = 4.3

ppm). As the reaction progressed, the intensity of the terminal alkyne signal exhibited progressive attenuation until complete disappearance, confirming full consumption of the AK1 monomer.

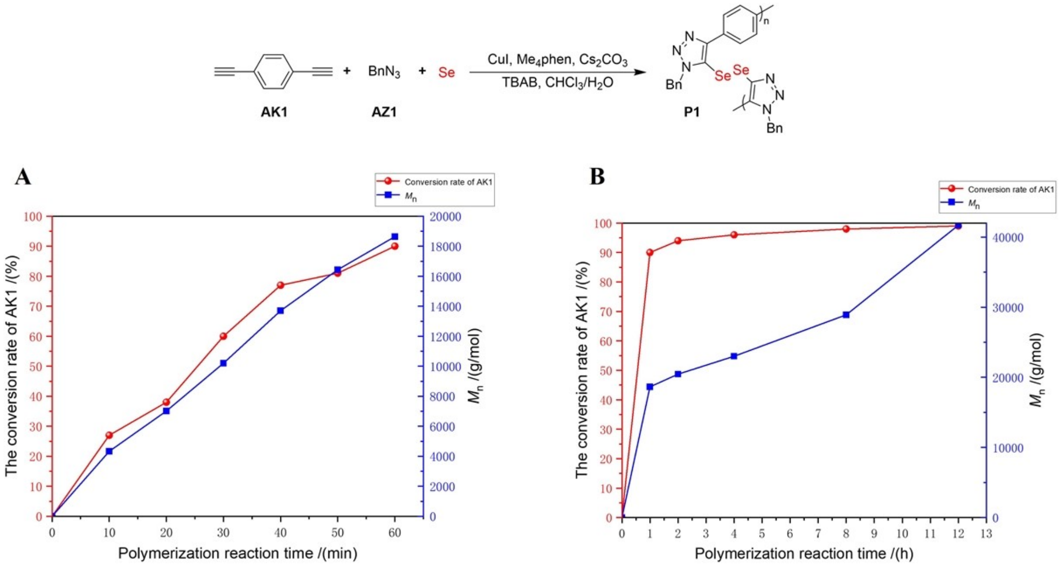


Figure S30. Short-Term (0-60 min) Kinetic Response Mechanisms in P1(A). Long-Term (0-12 h) Kinetic Response Mechanisms in P1(B).

14. Supplementary References.

1. X. Chen, A. Qin and B. Z. Tang, *Green Chem.*, 2024, **26**, 857-865.
2. L. Peng, Y. Zhao, Y. Okuda, L. Le, Z. Tang, S.-F. Yin, R. Qiu and A. Orita, *J. Org. Chem.*, 2023, **88**, 3089-3108.
3. B.-X. Sun, X.-N. Wang, T.-G. Fan, Y.-J. Hou, Y.-T. Shen and Y.-M. Li, *J. Org. Chem.*, 2023, **88**, 4528-4535.