Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Supramolecular polysulfide polymers cross-linked by metal-ligand interactions

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General information

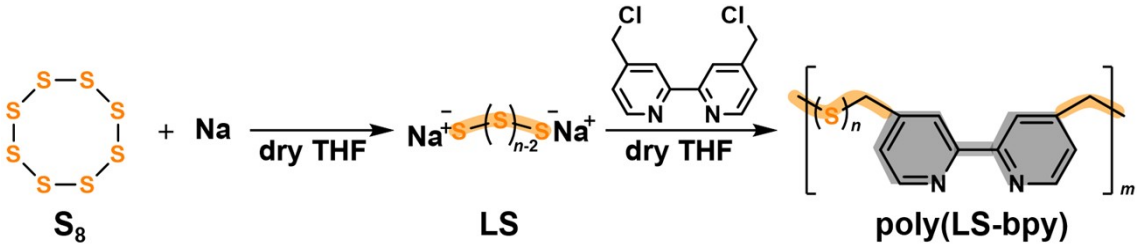
Materials.

All of the reagents and chemicals used were obtained from commercial sources, unless otherwise noted. Sulfur was purified by recrystallization from carbon disulfide.

Measurements.

The NMR spectra were obtained using a JEOL JNM-ECS 400 and 500 MHz NMR spectrometer. MALDI–TOF MS spectra were recorded in the linear positive mode on a mass spectrometer (BRUKER DALTONICS, Ultraflex III and autoflex maX). 2,5-Dihydroxybenzoic acid was used as a matrix. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) measurements. GPC measurements were performed with 10 mmol LiBr in DMSO (0.40 $mL \cdot min^{-1}$, 40 °C) using a TOSOH HLC-8320GPC EcoSEC® (TOSOH, Tokyo, Japan) equipped with a TOSOH TSK gel α-M column. UV-Vis measurements were performed using a JASCO V-650 spectrometer at room temperature. The thermogravimetric analysis was carried out from room temperature to 500 °C at a heating rate of 10 °C min^{-1} using a Rigaku Instrument Thermo Plus TG8120 in a N_2 atmosphere. Differential scanning calorimetry (DSC) was carried out with a Seiko Instruments DSC 6220 under a N_2 atmosphere and 10 K min^{-1} heating rate. Pyrolysis-GC-MS analysis was performed using a PY-2020iD pyrolyser (Frontier Laboratories Ltd.) connected to 6890 GC (Agilent Technologies International Japan, Ltd.) and JMS700 MS (JEOL). Pyrolysis was performed at a temperature of 100 °C. The purge flow of nitrogen to remove any oxygen from the sample, prior to pyrolysis, was set to 20 ml/min. The mass spectrometer ion source was set to 230 °C and the interface to 280 °C, scanning took place once per second in the range of 30 to 300 m/z..

1. Preparation of poly(LS-bpy)



Scheme S1. Preparation of poly(LS-bpy).

Sulfur (S_8) (1500 mg, 5.85 mmol) and sodium (Na) (278 mg, 12.1 mmol) were added to dry THF (60 mL) and the mixture was stirred at 75 ºC for 24 h. 4-(Chloromethyl)-4'-methyl-2,2'-bipyridyl (bpydiCl) (1720 mg, 6.81 mmol) was added to the suspension and the mixture was stirred at r.t. for 24 h. The resulting solution was filtered, H_2O and $CHCl_3$ were added to the filtrate, and the $CHCl_3$ layer was extracted. After drying the $CHCl_3$ with $MgSO_4$, the solution was filtered and filtrate was evaporated. The resulting sample was purified by separation GPC to obtain poly(LS-bpy). (40% Yield from S_8)

Table S1. Preparation of poly(LS-bpy)

	S_8 (mg / mmol)	Na (mg / mmol)	S_8 : Na	bpydiCl (mg / mmol)	S in poly(LS-bpy)	Yield (%)	M_n
Run 1	1500 / 5.86	278 / 12.0	1 : 2	1720 / 6.80	41	40	2,500
Run 2	500 / 1.95	137 / 5.96	1 : 3	726 / 2.87	34	32	2,700
Run 3	200 / 0.78	73 / 3.17	1 : 4	870 / 3.44	29	46	2,600
Run 4	200 / 0.78	144 / 6.25	1 : 8	1739 / 6.88	22	51	1,600
Run 5	500 / 3.94	89 / 3.91	1 : 2	741 / 2.93	40	28	2,600
Run 6	500 / 3.94	92 / 4.00	1 : 2	988 / 3.91	38	41	2,700
Run 7	500 / 3.94	91 / 3.94	1 : 2	1482 / 5.86	34	40	2,200

Data of poly(LS-bpy).

Physical State; Yellow powder.

Anal. Calcd. for $(C_{12}H_{10}N_2S_4)_n$: C 46.42, H 3.25, N 9.02, S 41.12 Found: C 46.67, H 3.39, N 8.82, S 41.31.

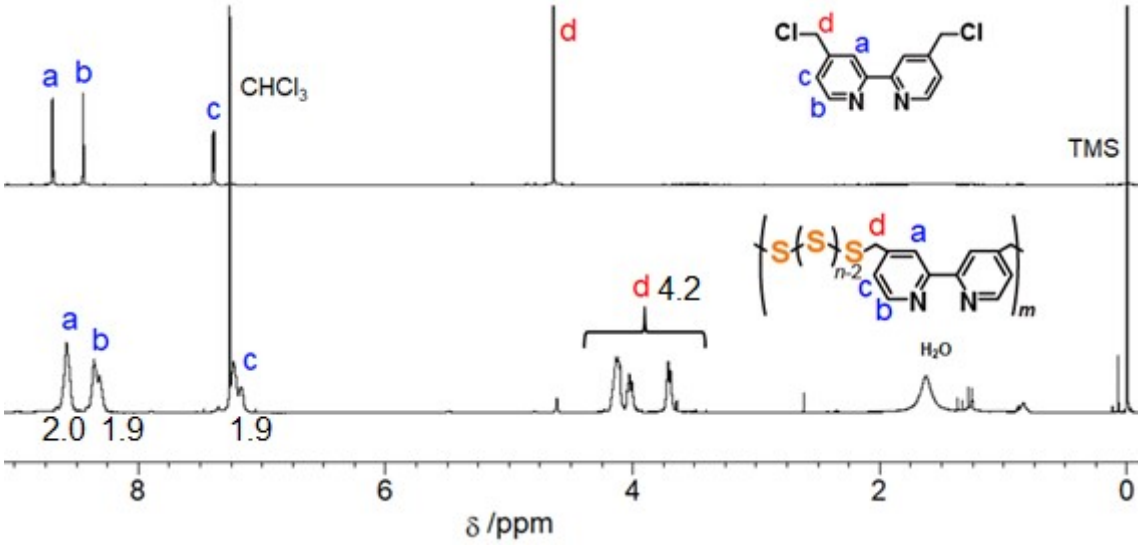


Figure S1. ^{1}H NMR spectra of bpydiCl (upper) and poly(LS-bpy) (bottom) in $CDCl_3$ at 30 °C.

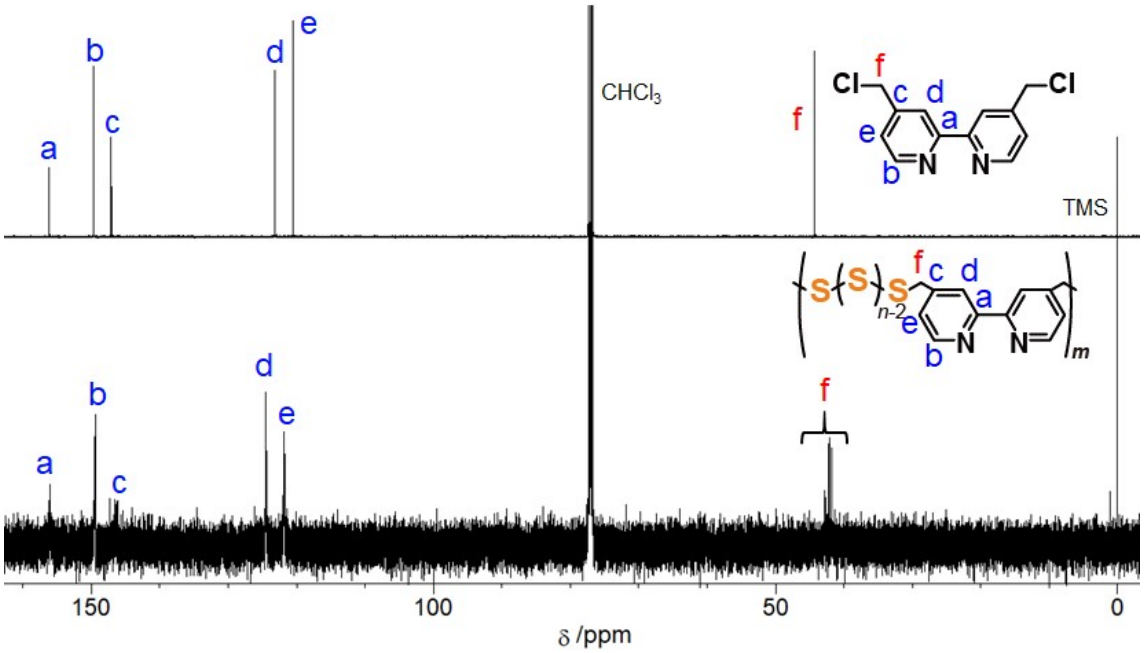


Figure S2. ^{13}C NMR spectra of bpydiCl (upper) and poly(LS-bpy) (bottom) in $CDCl_3$ at 30 °C.

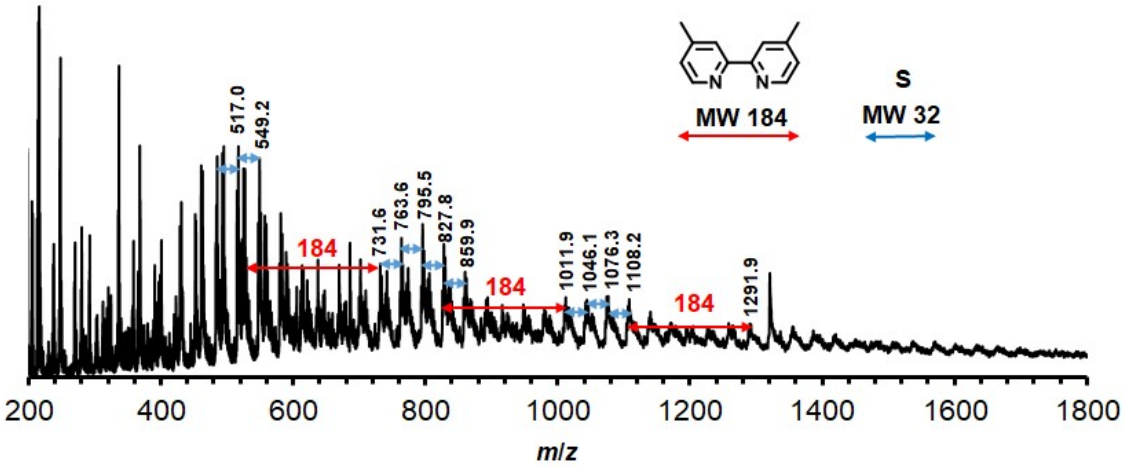


Figure S3. MALDI-TOF MS spectrum of poly(LS-bpy). Peaks for a number of the repeating unit of bpy (*m*/*z* 184) and sulfur (32) could be detected.

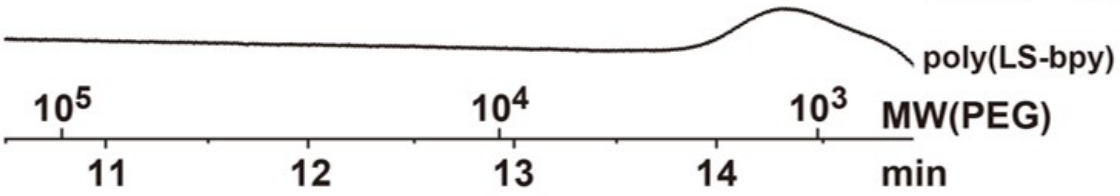
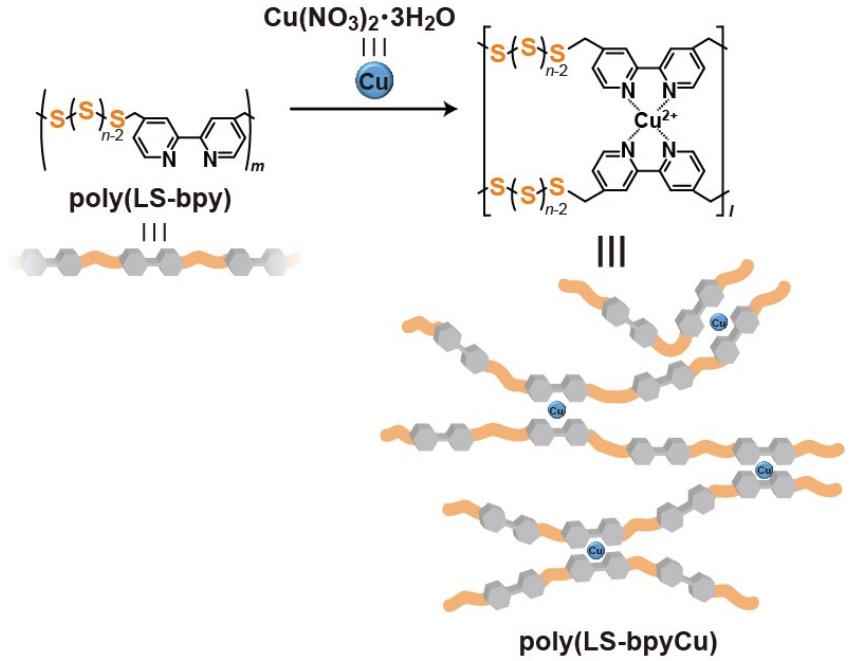
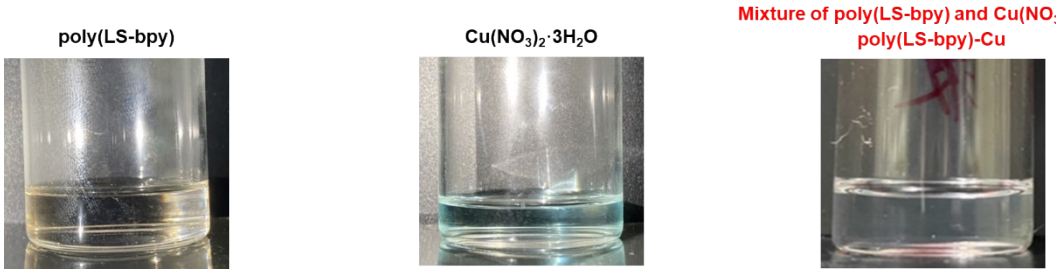


Figure S4. GPC profiles of poly(LS-bpy). The GPC measurement was performed in 0.1 wt% LiBr in DMSO solution at 40 °C. Molecular weight are based on the calibration of polyethylene glycol (PEG) standard.

2. Preparation of poly(LS-bpyCu)





Scheme S2. Preparation of poly(LS-bpyCu).

Poly(LS-bpy) (3.3 mg, 10.4 μmol (bpy part)) and copper(II) nitrate pentahydrate **[**$Cu(NO_3)_2 \cdot 5H_2O$**]** (1.3 mg, 5.2 μmol) were added to mixed solution of $CHCl_3$ (16.0 mL) and MeOH (4.0 mL), stirred at r.t. for 24 h, and the solution was removed to obtain poly(LS-(bpyCu).

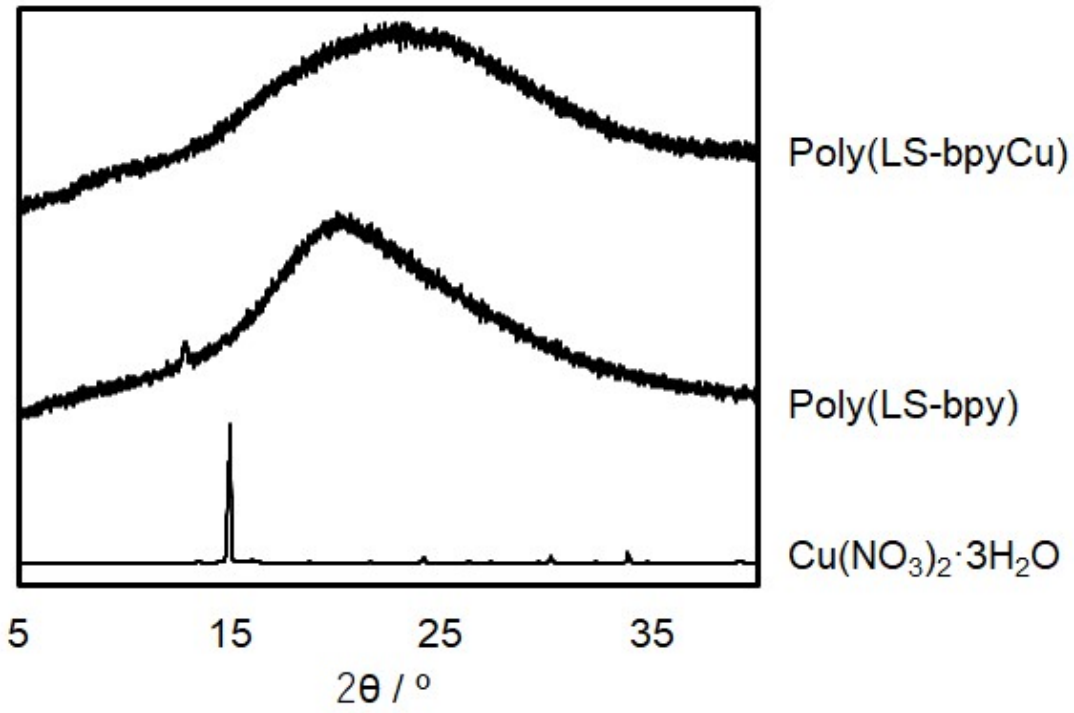


Figure S5. XRD patterns of $Cu(NO_3)_2 \cdot 5H_2O$, poly(LS-bpy), and poly(LS-bpyCu). Introduction of Cu(II) into the poly(LS-bpy) was confirmed by the absence of diffraction peaks for neat $Cu(NO_3)_2 \cdot 5H_2O$ in the XRPD measurement of poly(LS-bpyCu).

UV-Vis measurement

Poly(LS-bpyCu)

To confirm the complex formation of bpy part in poly(LS-bpy) and Cu(II), we performed the UV-Vis measurement of mixture of poly(LS-bpy) and $Cu(NO_3)_2 \cdot 3H_2O$. Mixed solution of $CHCl_3$ and MeOH (4:1) of 46.7 μM poly(LS-bpy) was prepared in a UV cuvette (1 cm path length). Aliquots (2.67 μL) of the mixed solution of $CHCl_3$ and MeOH (4:1) solution of 10.5 mM $Cu(NO_3)_2 \cdot 3H_2O$ were added to the solution of poly(LS-bpy) in the UV cuvette. After each aliquot addition, the solution was allowed to stand until the absorbance reached a constant value. A new peak appeared at 308 nm due to the addition of $Cu(NO_3)_2 \cdot 3H_2O$ (Fig. S5). This peak was also observed in mixture of bpy and $Cu(NO_3)_2 \cdot 3H_2O$ (Fig. S6). These results indicate that poly(LS-bpy) forms a complex by the coordination bond between bpy in poly(LS-bpy)$_2$ and Cu(II).

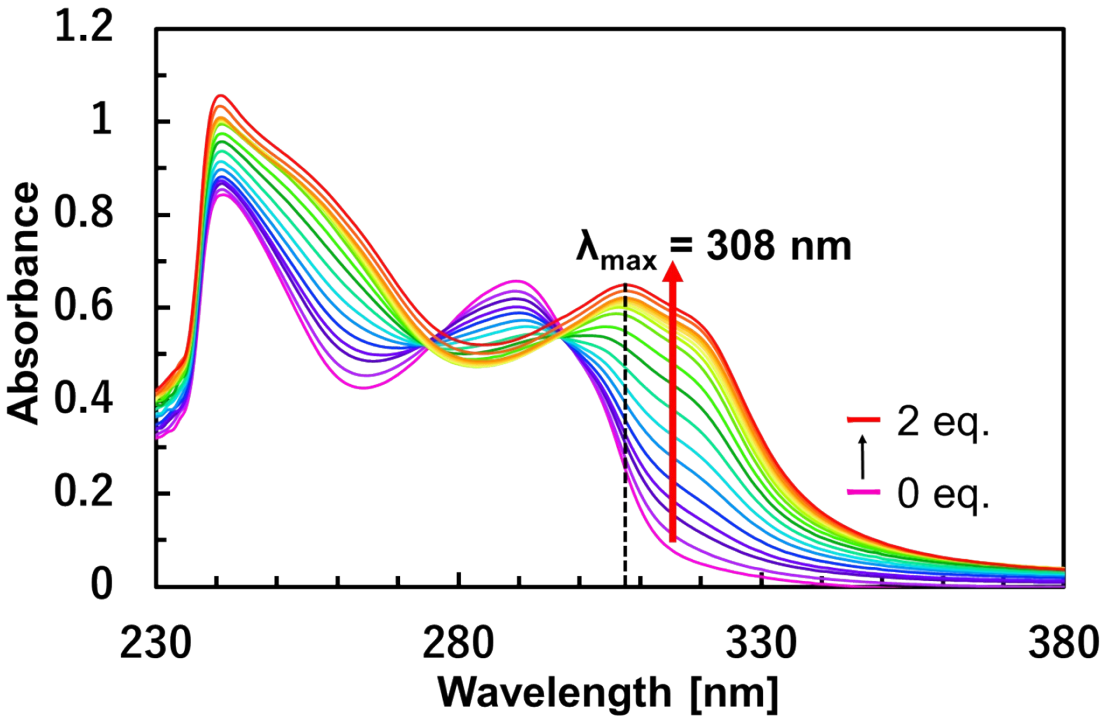


Figure S6. UV-Vis absorption spectra of addition of aliquots (2.67 μL) of 10.5 mM $Cu(NO_3)_2 \cdot 3H_2O$ $CHCl_3$/MeoH (4:1) solution to the 46.7 μM poly(LS-bpy) $CHCl_3$/MeOH (4:1) solution at 25 °C.

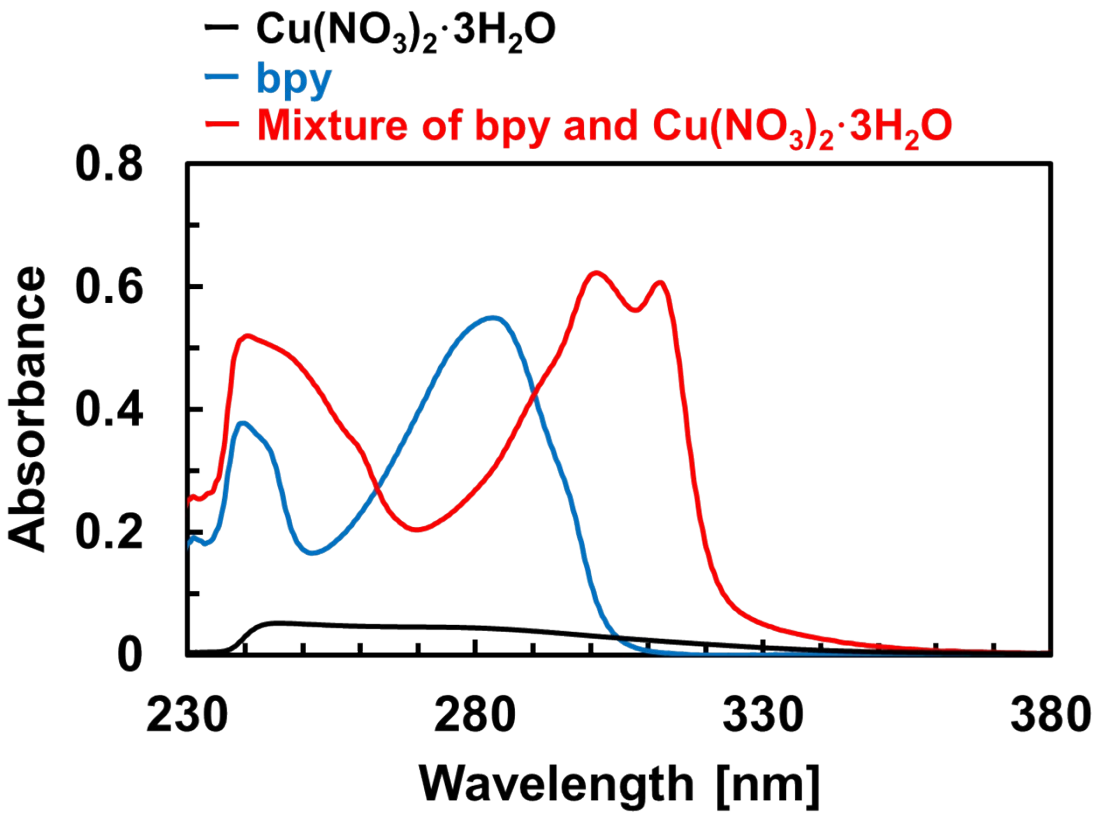
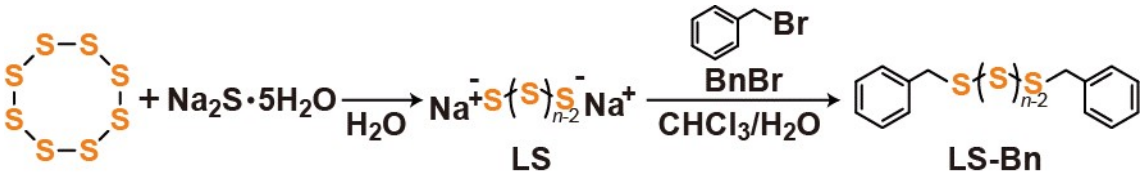


Figure S7. UV-Vis spectra of $Cu(NO_3)_2 \cdot 3H_2O$ (black), bpy (blue), and mixture of bpy and $Cu(NO_3)_2 \cdot 3H_2O$ (red) in $CHCl_3$/MeoH (4:1) at 25 °C. The concentrations of bpy and $Cu(NO_3)_2 \cdot 3H_2O$ were 40 μM and 14 μM, respectively.

3. Preparation of LS-Bn



Scheme S3. Preparation of LS-Bn.

S_8 (169.7 mg, 1.01 mmol) and benzyl bromide (BnBr, 480 μL, 4.04 mmol) were dissolved in a $Na_2S \cdot 5H_2O$ aqueous solution and $CHCl_3$, respectively. The two solutions were mixed and stirred at r.t. for 24 h. After the reaction, $CHCl_3$ was extracted and purified by silica column chromatography to obtain LS-Bn.

Data of LS-Bn.
Physical State; Orange oil.
Anal. Calcd. for $C_{14}H_{14}S_3$: C 60.39, H 5.07, S 34.54, Found: C 60.19, H 5.02, S 34.23.

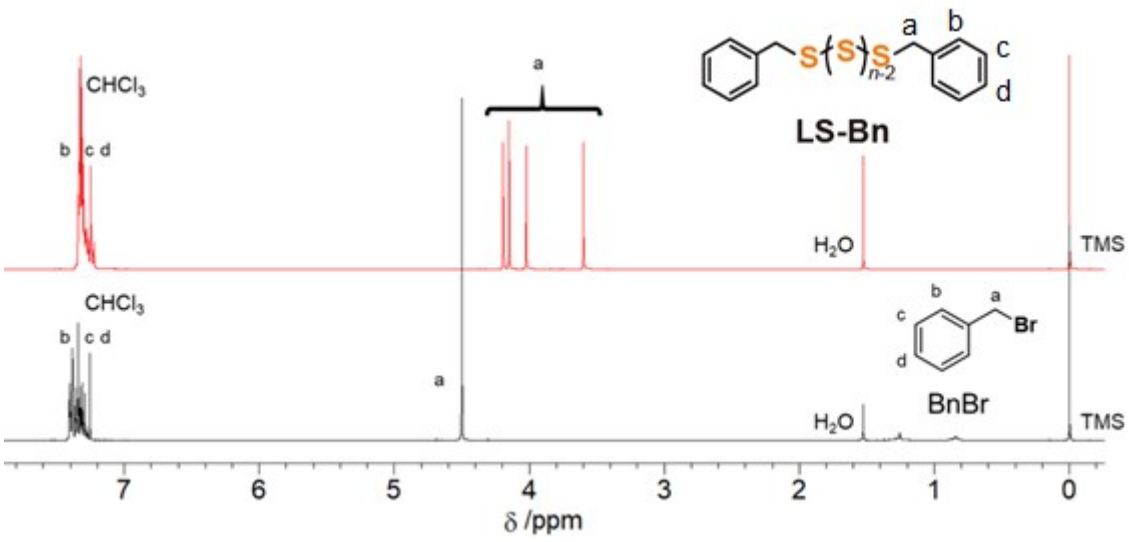


Figure S8. ^{1}H NMR spectra of LS-Bn (red) and BnBr (black).

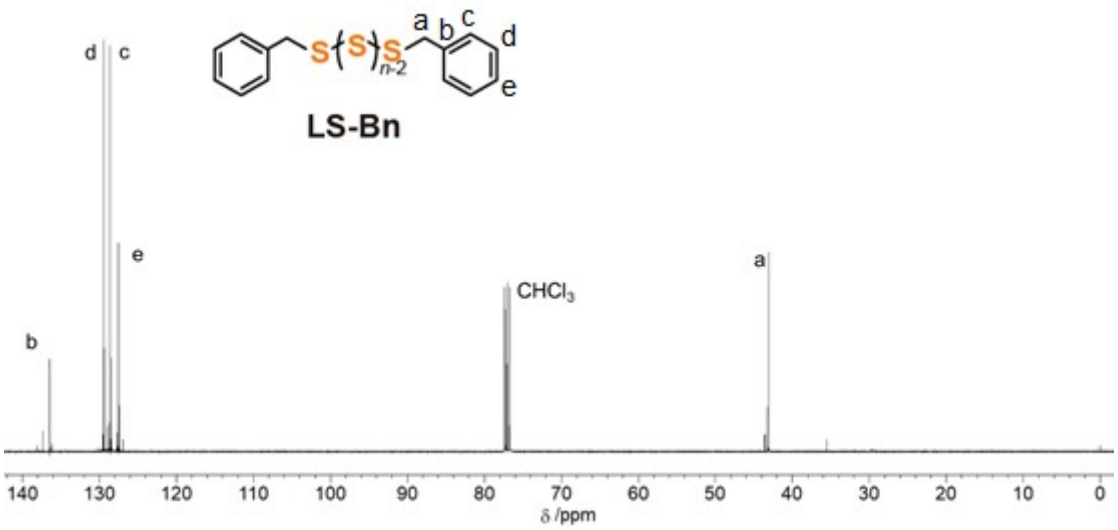


Figure S9. ^{13}C NMR spectrum of LS-Bn.

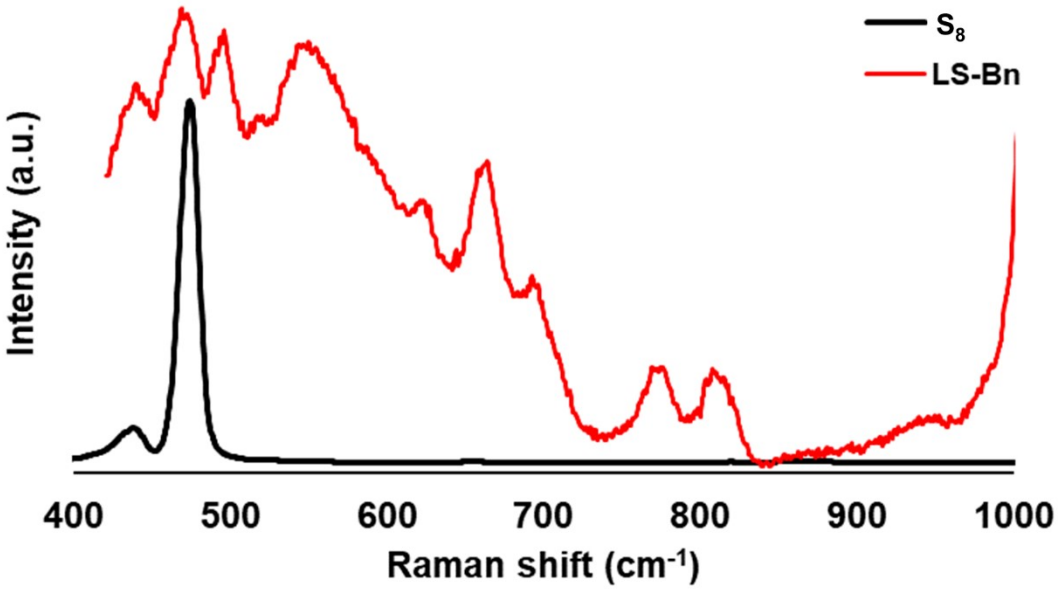


Figure S10. Raman spectra of S_8 (black) and LS-Bn (red).

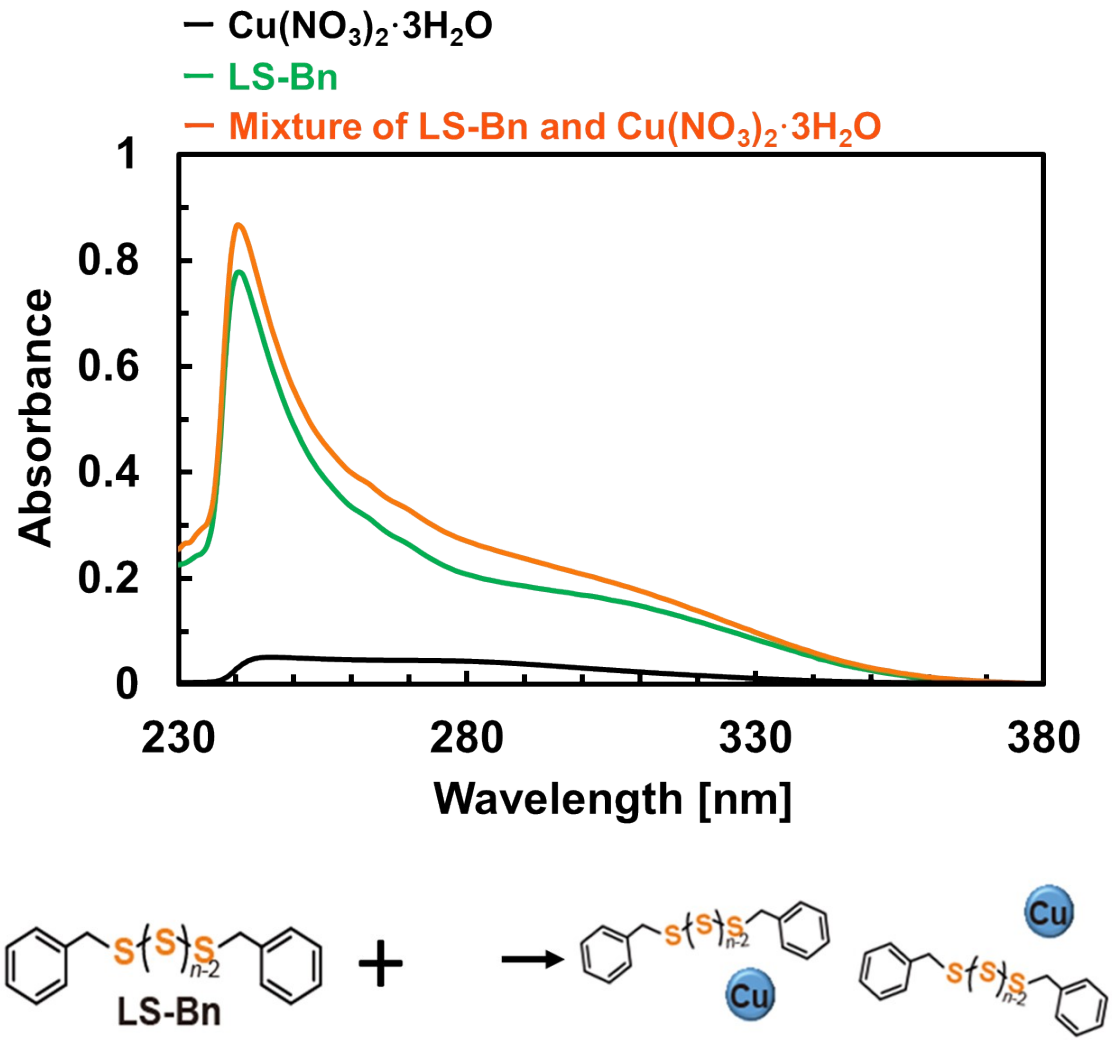
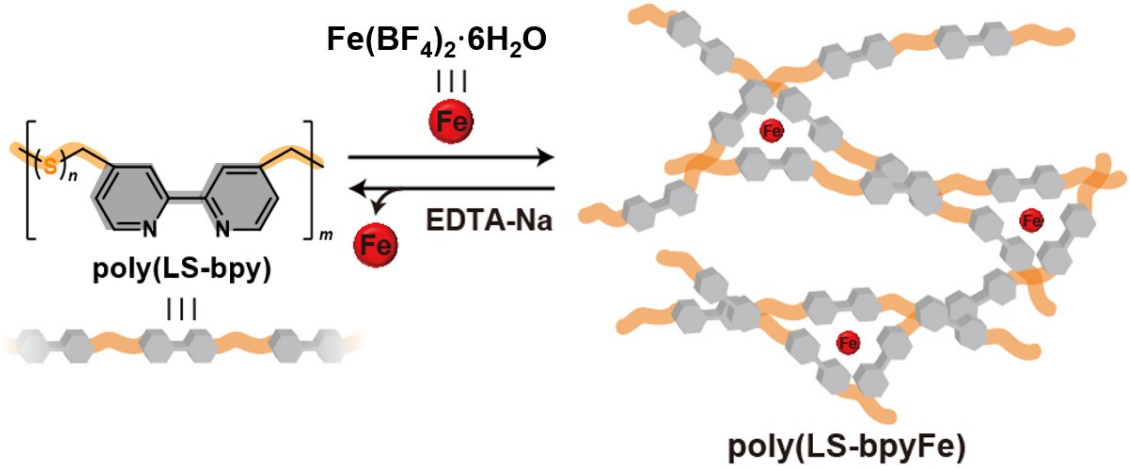


Figure S11. UV-Vis spectra of $Cu(NO_3)_2 \cdot 3H_2O$ (black), LS-Bn (green), and mixture of LS-Bn and $Cu(NO_3)_2 \cdot 3H_2O$ (orange) in $CHCl_3$/MeoH (4:1) at 25 °C. The concentrations of LS-Bn and $Cu(NO_3)_2 \cdot 3H_2O$ were 1.4 and 14 μM, respectively.

4. Preparation of Poly(LS-bpyFe)



Scheme S4. Preparation of poly(LS-bpyFe).

Poly(LS-bpy) (7.5 mg, 21.6 μmol (bpy part)) and Iron(II) tetrafluoroborate hexahydrate (**(**$Fe(BF_4)_2 \cdot 6H_2O$ (2.4 mg, 7.19 μmol) were added to mixed solution of $CHCl_3$ (16.0 mL) and MeOH (4.0 mL) and stirred at r.t. for 24 h. Precipitation occurred in the solution during the reaction. The precipitate was collected and dried to obtain poly(LS-(bpyFe).

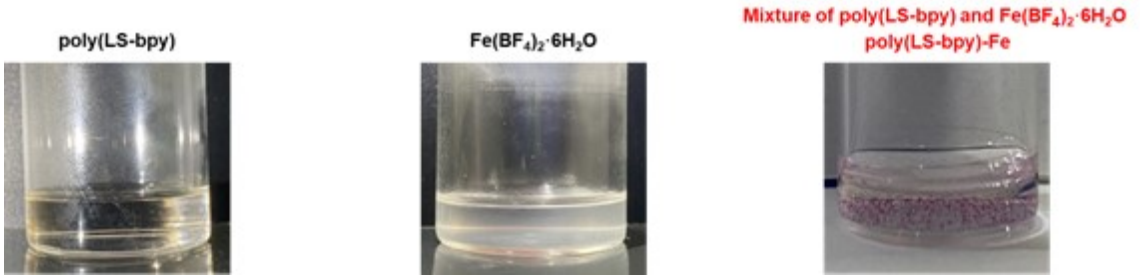


Figure S12. Photographs of poly(LS-bpy) (left), $Fe(BF_4)_2 \cdot 6H_2O$ (center), and mixture of poly(LS-bpy) and $Fe(BF_4)_2 \cdot 6H_2O$ (poly(LS-bpyFe)) (right) in $CHCl_3$/MeOH (4:1), respectively.

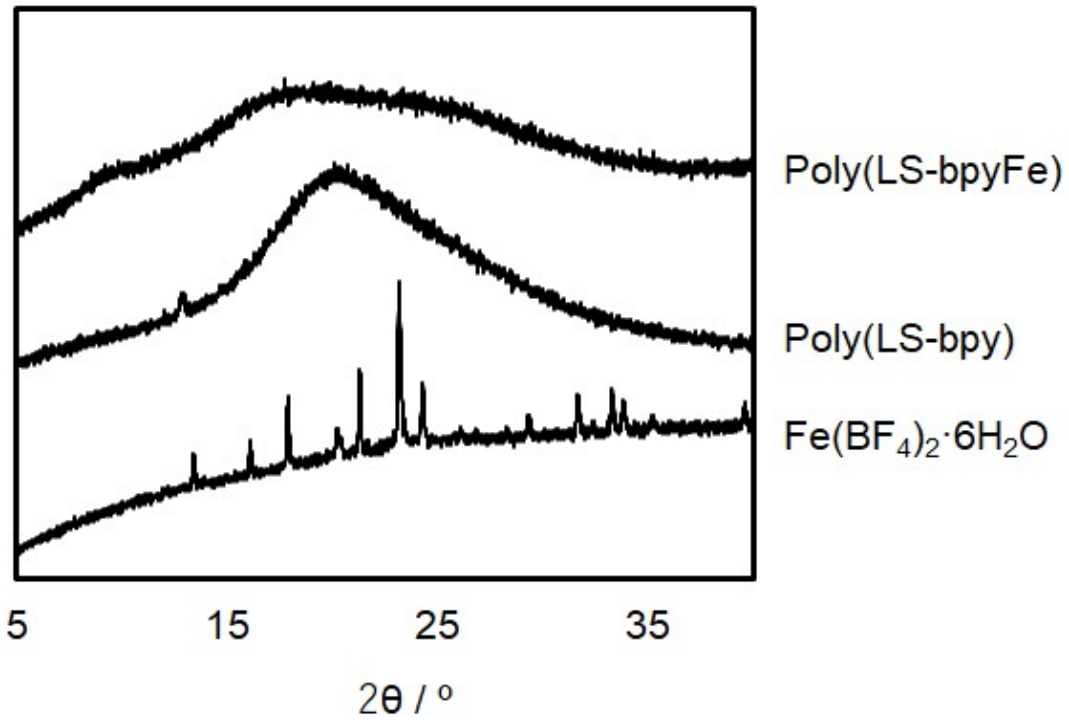


Figure S13. XRD patterns of $Fe(BF_4)_2 \cdot 6H_2O$, poly(LS-bpy), and poly(LS-bpyFe). Introduction of Fe(II) into the poly(LS-bpy) was confirmed by the absence of diffraction peaks for neat $Fe(BF_4)_2 \cdot 6H_2O$ in the XRPD measurement of poly(LS-bpyFe).

UV-Vis measurement

Poly(LS-bpyFe)

To confirm the complex formation of bpy part in poly(LS-bpy) and Fe(II), we performed the UV-Vis measurement of mixture of poly(LS-bpy) and $Cu(NO_3)_2 \cdot 3H_2O$. Mixed solution of $CHCl_3$ and MeOH (4:1) of 46.7 μM poly(LS-bpy) was prepared in a UV cuvette (1 cm path length). Aliquots (2.32 μL) of the mixed solution of $CHCl_3$ and MeOH (4:1) solution of 6.04 mM $Fe(BF_4)_2 \cdot 6H_2O$ were added to the solution of poly(LS-bpy) in the UV cuvette. After each aliquot addition, the solution was allowed to stand until the absorbance reached a constant value. A new peak appeared at 545 nm due to the addition of $Fe(BF_4)_2 \cdot 6H_2O$ (Fig. S12). This peak was also observed in mixture of bpy and $Fe(BF_4)_2 \cdot 6H_2O$ (Fig. S13). These results indicate that poly(LS-bpy) forms a complex by the coordination bond between bpy in poly(LS-bpy) and Fe.

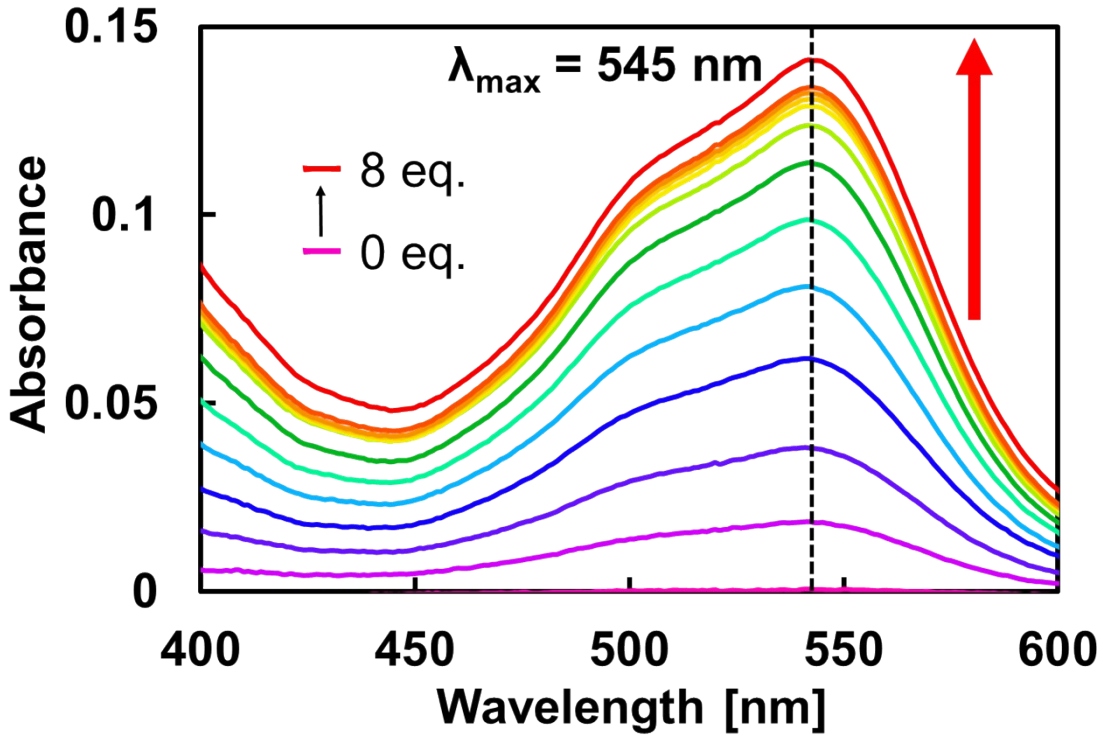


Figure S14. UV-Vis absorption spectra of addition of aliquots (2.32 μL) of 6.04 mM $Fe(BF_4)_2 \cdot 6H_2O$ $CHCl_3$/MeOH (4:1) solution to the 46.7 μM poly(LS-bpy) $CHCl_3$/MeoH (4:1) solution at 25 °C.

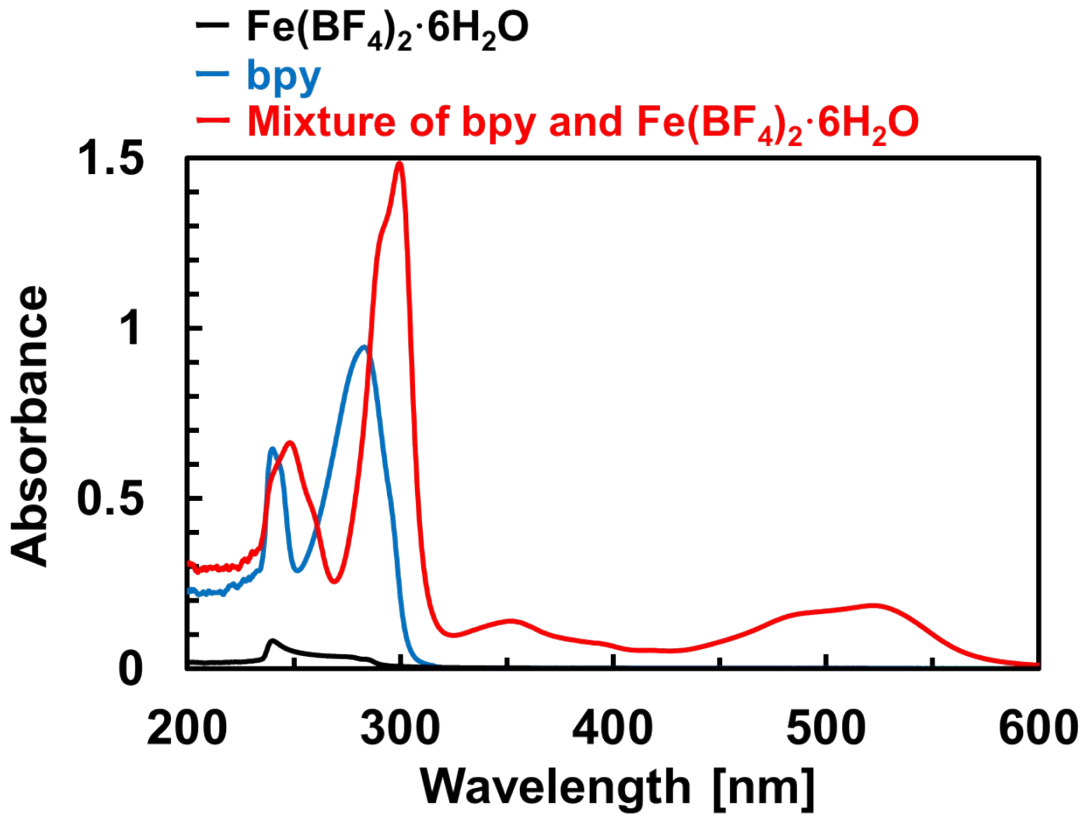


Figure S15. UV-Vis spectra of $Fe(BF_4)_2 \cdot 6H_2O$ (black), bpy (blue), and mixture of bpy and $Fe(BF_4)_2 \cdot 6H_2O$ (red) in $CHCl_3$/MeoH (4:1) at 25 °C. The concentrations of bpy and $Fe(BF_4)_2 \cdot 6H_2O$ were 66.7 μM and 7.55 mM, respectively.

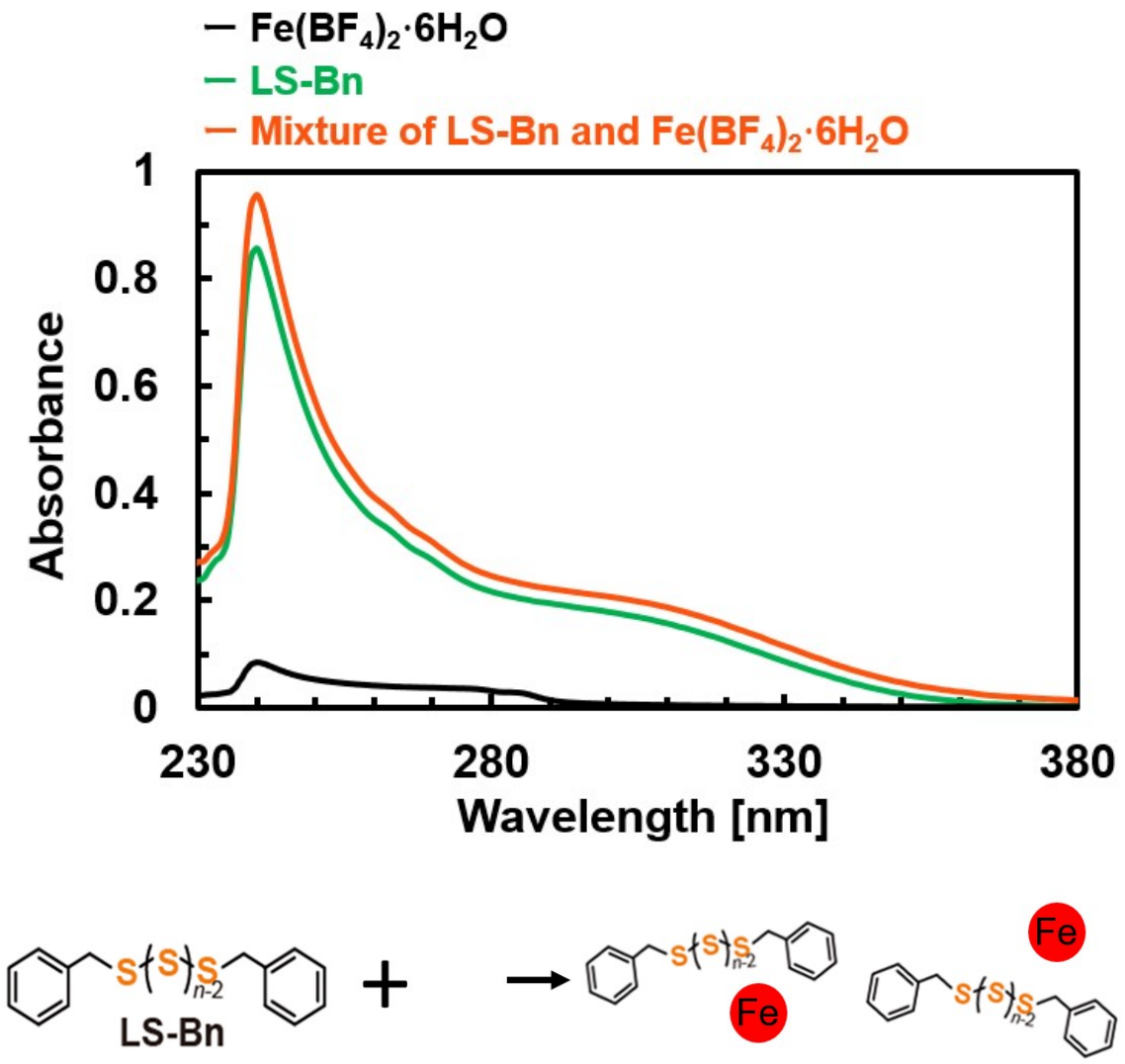


Figure S16. UV-Vis spectra of $Cu(NO_3)_2 \cdot 3H_2O$ (black), LS-Bn (green), and mixture of LS-Bn and $Cu(NO_3)_2 \cdot 3H_2O$ (red) in $CHCl_3$/MeOH (4:1) at 25 °C. The concentrations of LS-Bn and $Cu(NO_3)_2 \cdot 3H_2O$ were 47.5 and 7.55 μM, respectively.

5. Disassembly and re-assembly of poly(LS-bpyCu)

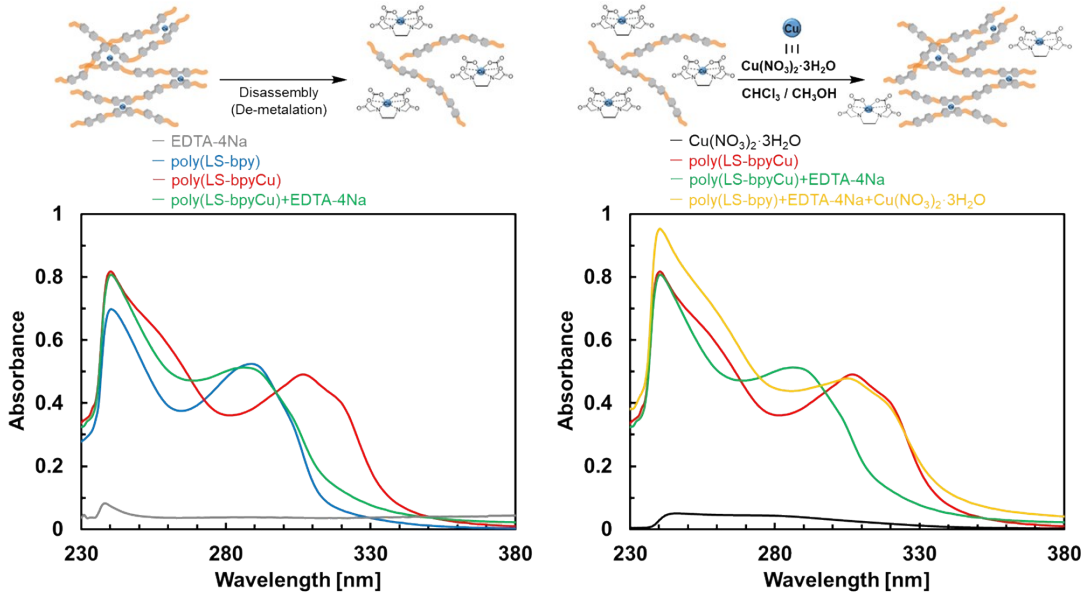


Figure S17. UV-Vis spectra of EDTA-Na (gray), 46.7 μM poly(LS-bpy) (blue), 40 μM poly(LS-bpyCu) (red), a mixture of poly(LS-bpyCu) and 10 eq. of EDTA-Na (green), 14 μM $Cu(NO_3)_2 \cdot 5H_2O$ (black), and re-assembled poly(LS-bpyCu) where 0.6 eq. of $Cu(NO_3)_2 \cdot 5H_2O$ was added to the filtrate of the mixture of poly(LS-$(bpy)_2$Cu) and EDTA-Na (orange) in $CHCl_3/CH_3OH$ = 4:1 solution. The increase in the overall absorbance in the UV-Vis spectra is due to the absorption of EDTA-Na or $Cu(NO_3)_2 \cdot 3H_2O$. For samples with Abs. greater than 1, the samples were diluted and measured to reduce absorbance to ~1.

6. DSC and TGA of poly(LS-bpyCu)

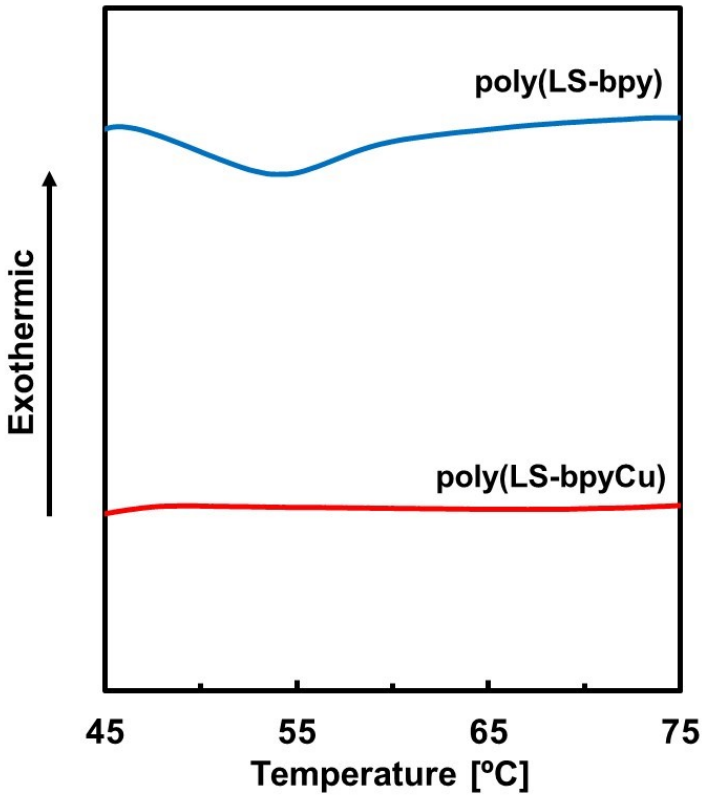


Figure S18. DSC profiles of poly(LS-bpy) (blue) and poly(LS-bpyCu) (red).

In the TG profiles, the weight loss of poly(LS-bpyCu) was in two steps, 95 and 249 °C. Pyrolysis-GC-MS measurements were performed at 100 °C to investigate the compounds decomposing in the first step. In the pyrolysis-GC-MS profiles of poly(LS-bpyCu), a peak of O_2 (m/z = 32) when nitric acid decomposes was observed (Fig. S17). The peak of O_2 (m/z = 32) was also observed in the pyrolysis-GC-MS profiles of nitric acid (Fig S18). These results indicated that the weight loss in the first step was due to nitrate ions coordinated to Cu(II). The decomposition temperature of poly(LS-bpyCu) was higher than that of poly(LS-bpy).

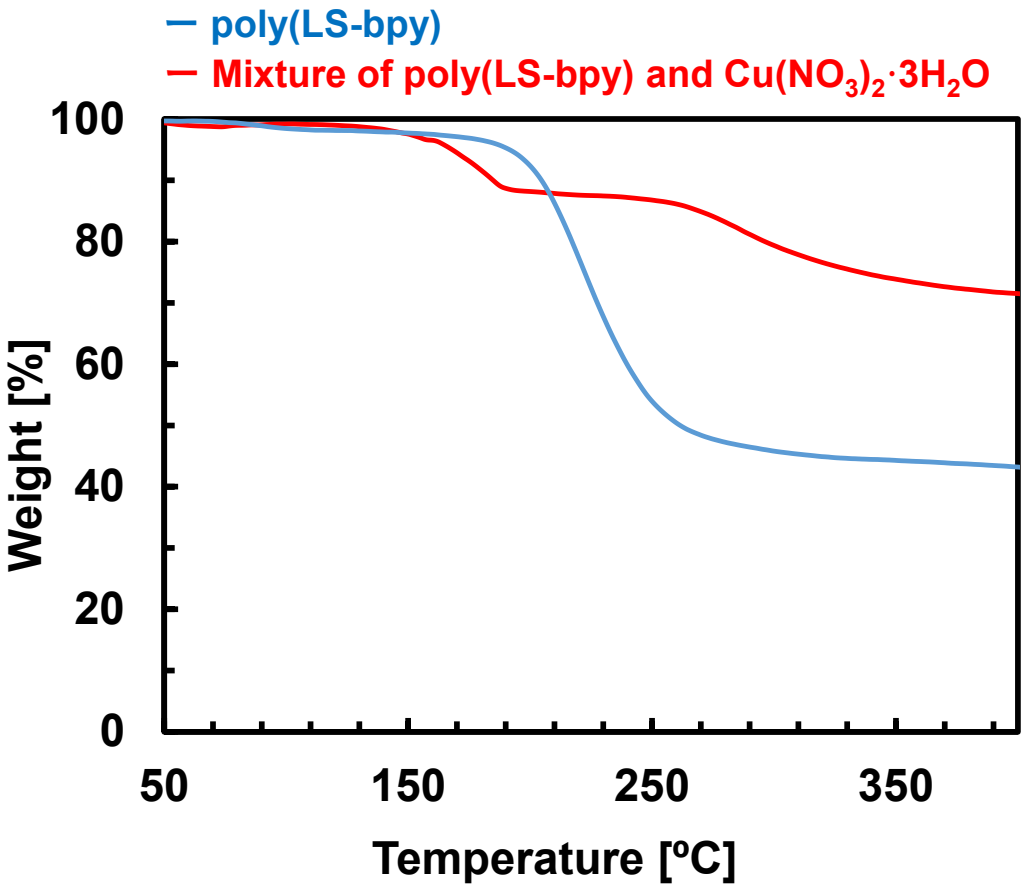


Figure S19. TG profiles of poly(LS-bpy) (blue) and poly(LS-bpyCu) (red).

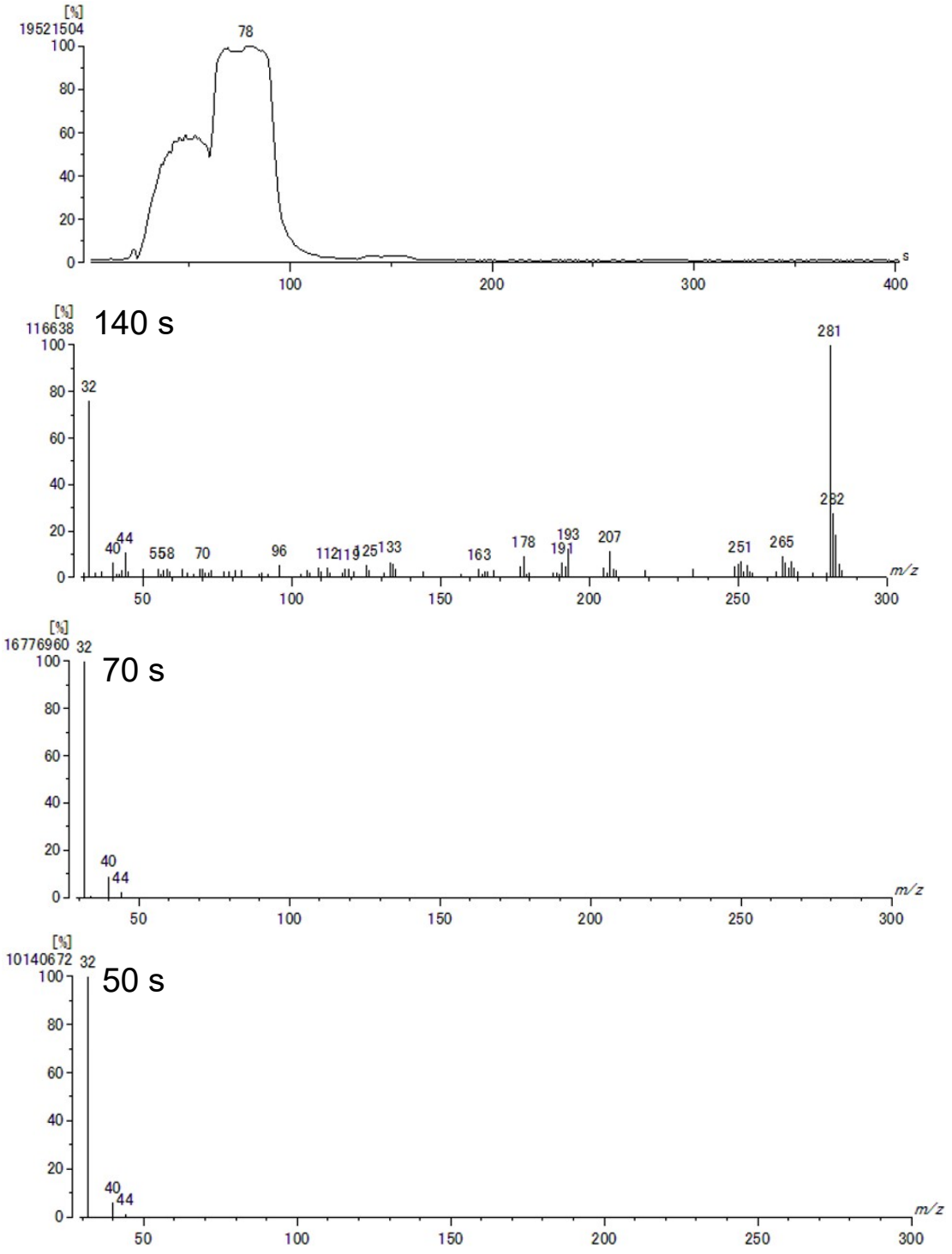


Figure S20. Pyrolysis-GC-MS profiles of poly(LS-bpyCu).

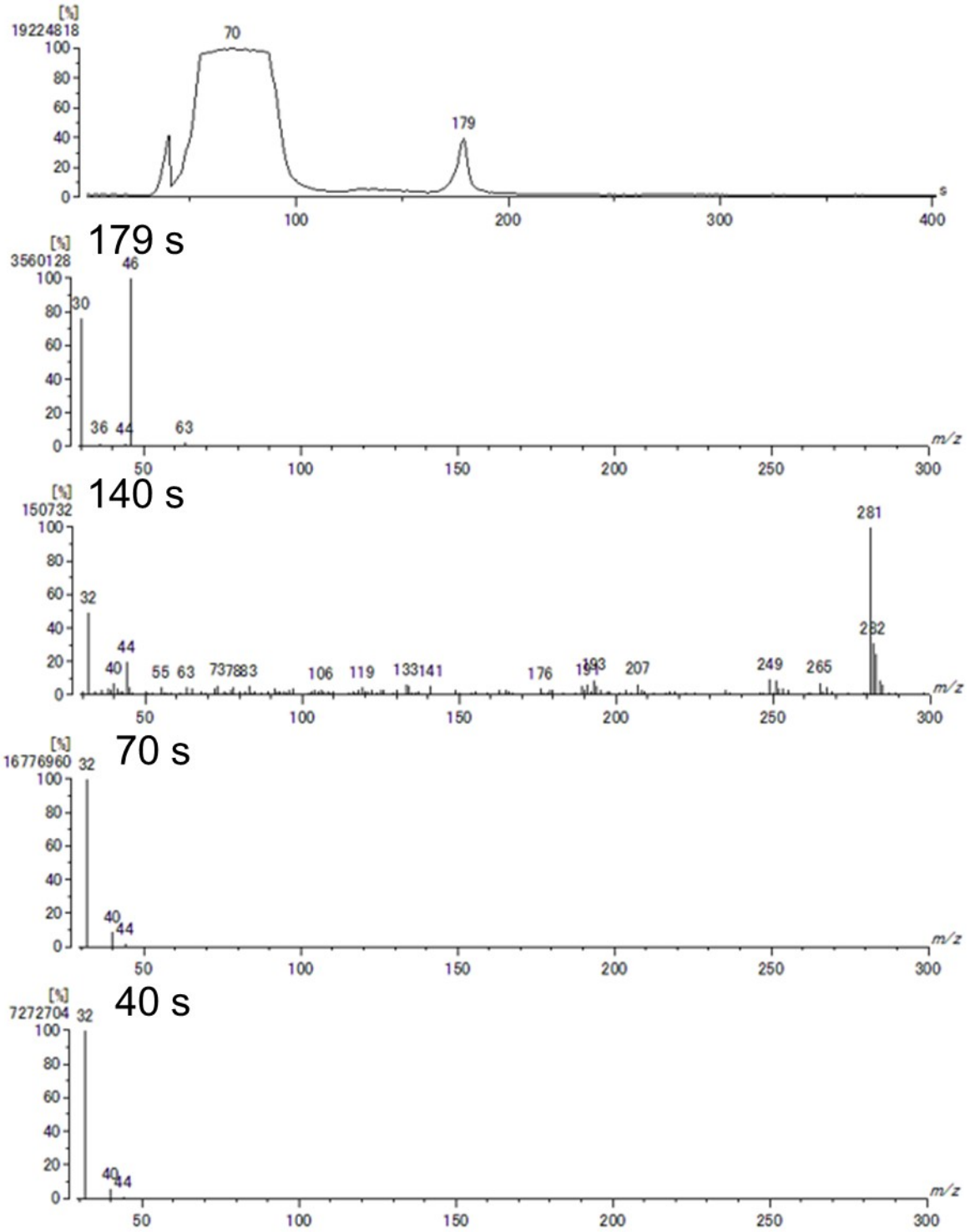


Figure S21. Pyrolysis-GC-MS profiles of nitric acid.