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NMR data

2-Bromo-3-methoxythiophene (**1**)

^{1}H NMR(400 MHz, $CDCl_3$, ppm) δ= 7.21 (d , 1H , J = 6.0 Hz), 6.77 (d , 1H , J = 6.0 Hz), 3.90 (s , 3H)

^{13}C NMR(100 MHz, $CDCl_3$, ppm) δ=155.3, 124.4, 116.4, 90.7, 59.3

2-Iodo-3-methoxythiophene (**2**)

It was difficult to isolate pure compound **2** due to the instability.

2-Chloro-3-methoxythiophene (**3**)

^{1}H NMR(400 MHz, $CDCl_3$, ppm) δ= 7.02 (d, J = 6.2 Hz, 1H), 6.79 (d, J = 6.2 Hz, 1H), 3.90 (s, 3H)

^{13}C NMR(100 MHz, $CDCl_3$, ppm) δ= 153.1, 120.9, 116.5, 107.6, 59.3

3-Methoxythiophene (**4**)

^{1}H NMR(400 MHz, $CDCl_3$, ppm) δ= 7.17 (dd, J=5.2, 3.2 Hz, 1H), 6.75 (dd, J=5.2, 1.6 Hz, 1H), 6.24 (dd, J=3.2, 1.6 Hz, 1H) 3.80 (s, 3H)

^{13}C NMR(100 MHz, $CDCl_3$, ppm) δ= 158.9, 124.9, 119.4, 96.7, 57.5

2,5-Dibromo-3-methoxythiophene (**5**)

^{1}H NMR(400 MHz, $CDCl_3$, ppm) δ= 3.86 (s, 3H), 6.79 (s, 1H)

^{13}C NMR(100 MHz, $CDCl_3$, ppm) δ=154.5, 119.9, 109.9, 89.6, 59.5

3-Bromo-2-methoxythiophene (**6**)

^{1}H NMR(400 MHz, $CDCl_3$, ppm) δ= 6.76 (d, J = 6.0 Hz, 1H), 6.65 (d, J = 6.0 Hz, 1H), 3.97 (s, 3H)

^{13}C NMR(100 MHz, $CDCl_3$, ppm) δ=159.0, 127.9, 112.2, 91.6, 62.3

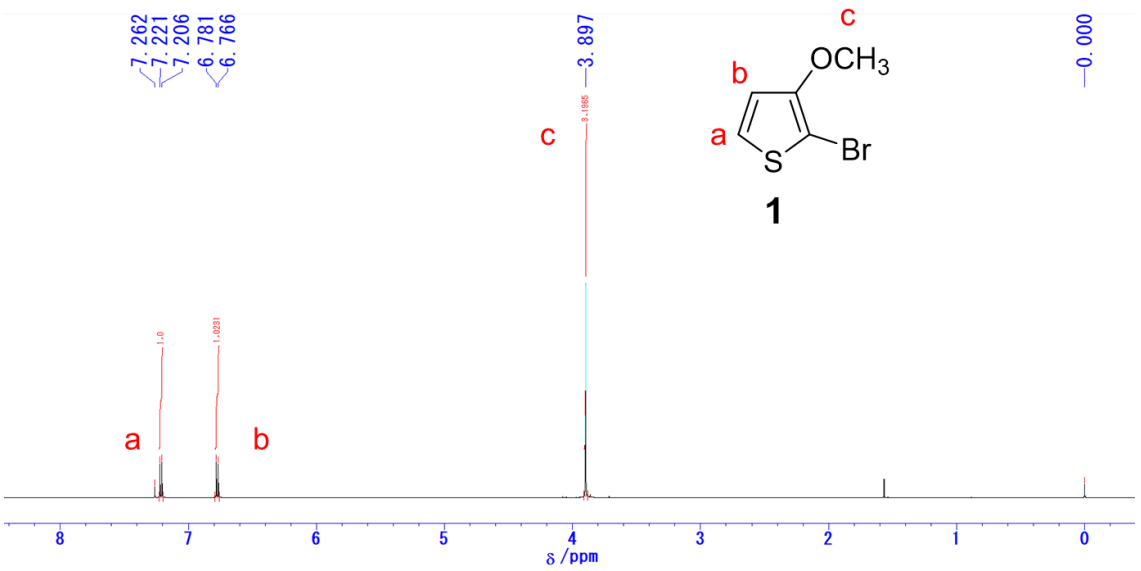


Figure S1 ^{1}H NMR spectrum of the 2-bromo-3-methoxythiophene (**1**). (400 MHz, $CDCl_3$)

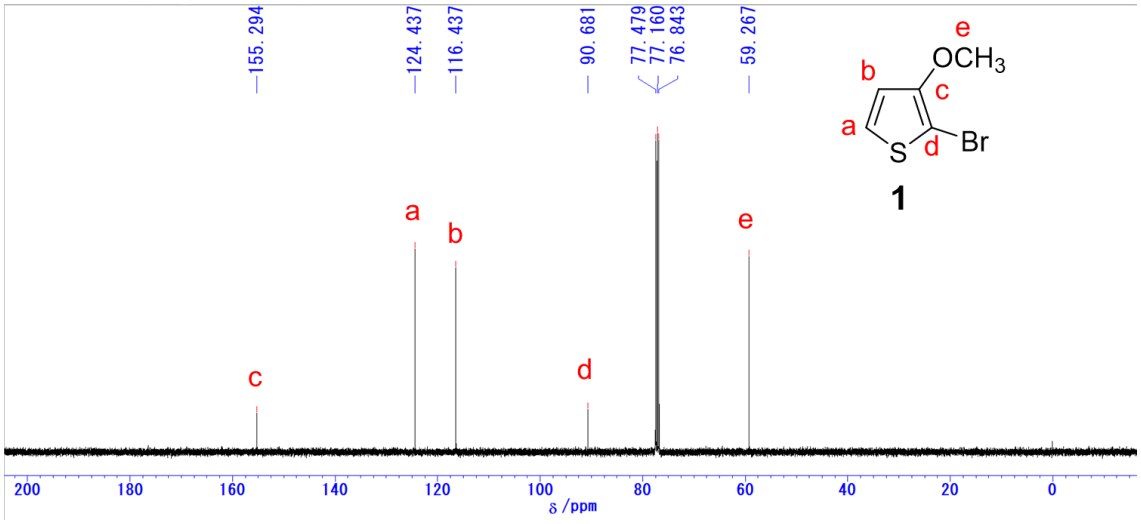


Figure S2 ^{13}C NMR spectrum of the 2-bromo-3-methoxythiophene (**1**). (100 MHz, $CDCl_3$)

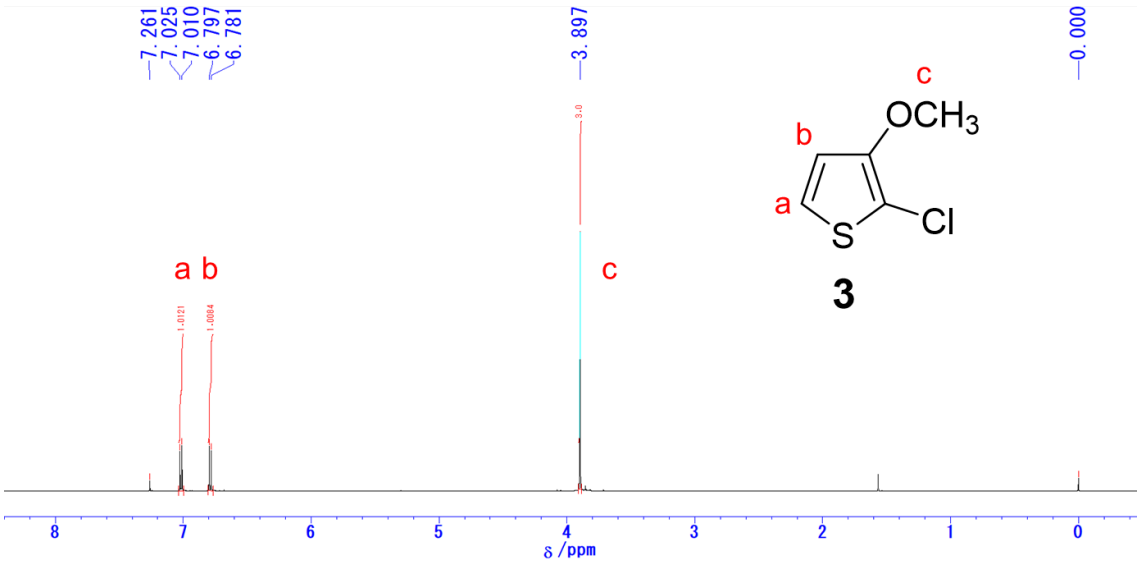


Figure S3 ^{1}H NMR spectrum of the 2-chloro-3-methoxythiophene (**3**). (400 MHz, $CDCl_3$)

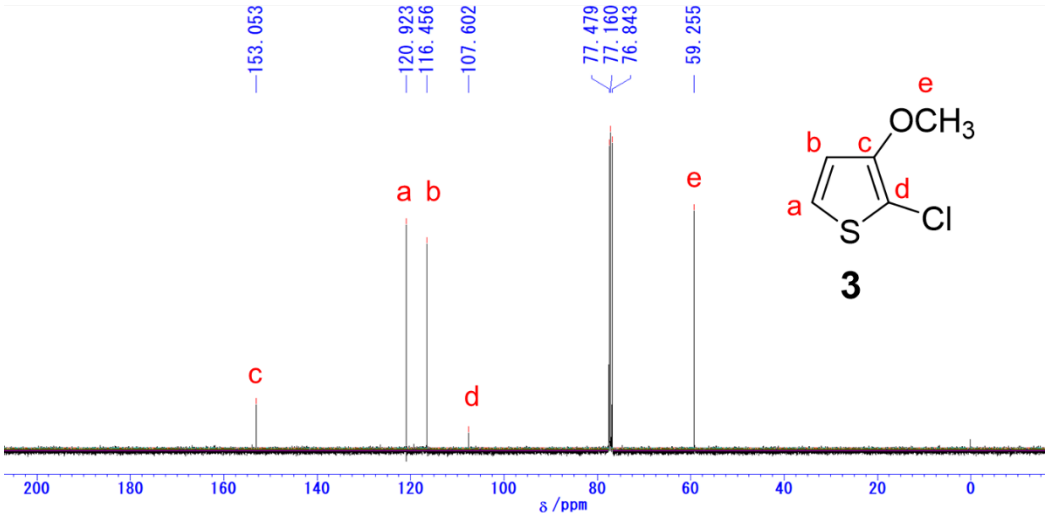


Figure S4 ^{13}C NMR spectrum of the 2-chloro-3-methoxythiophene (**3**). (100 MHz, $CDCl_3$)

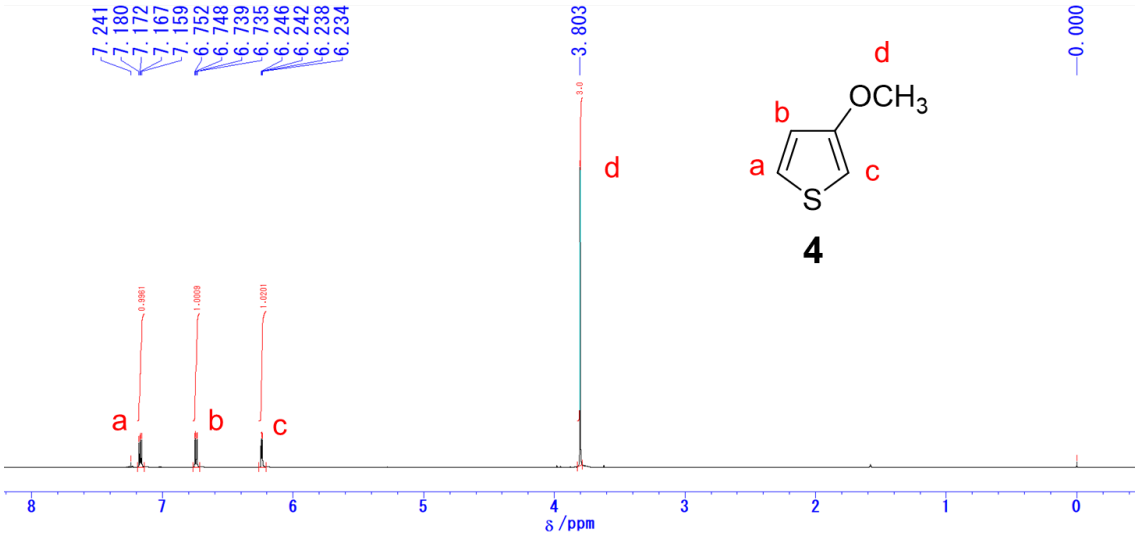


Figure S5 ^{1}H NMR spectrum of the 3-methoxythiophene (**4**). (400 MHz, $CDCl_3$)

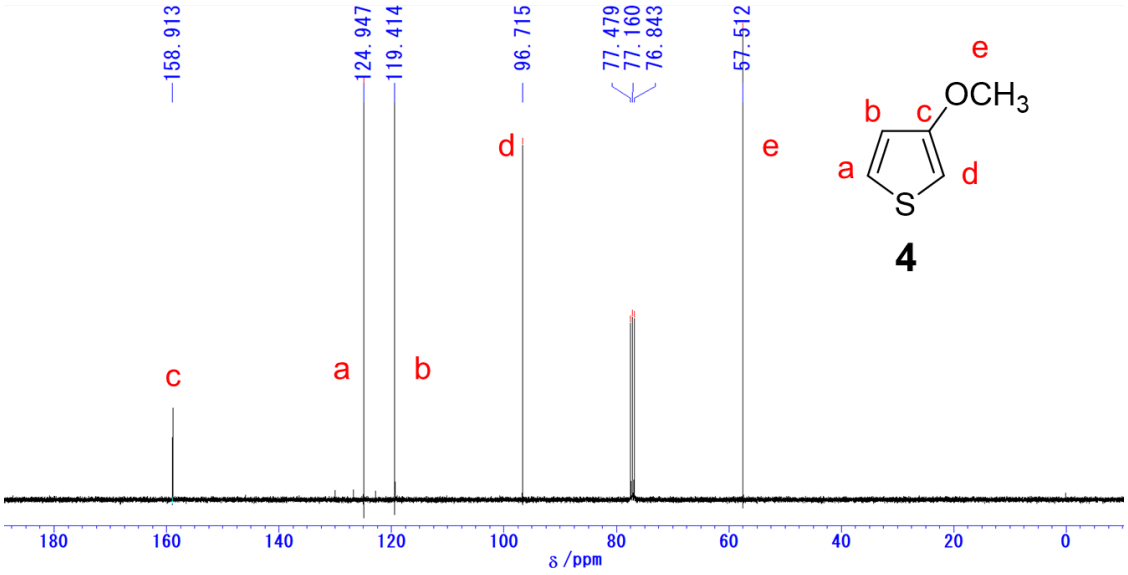


Figure S6 ^{13}C NMR spectrum of the 3-methoxythiophene (**4**). (100 MHz, $CDCl_3$)

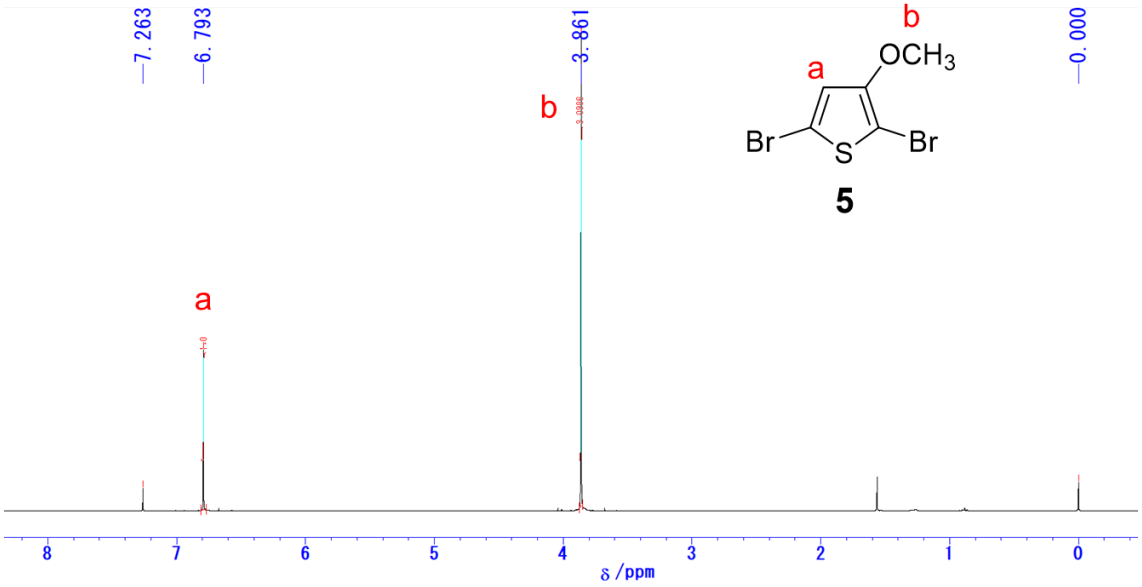


Figure S7 ^{1}H NMR spectrum of the 2,5-dibromo-3-methoxythiophene (**5**). (400 MHz, $CDCl_3$)

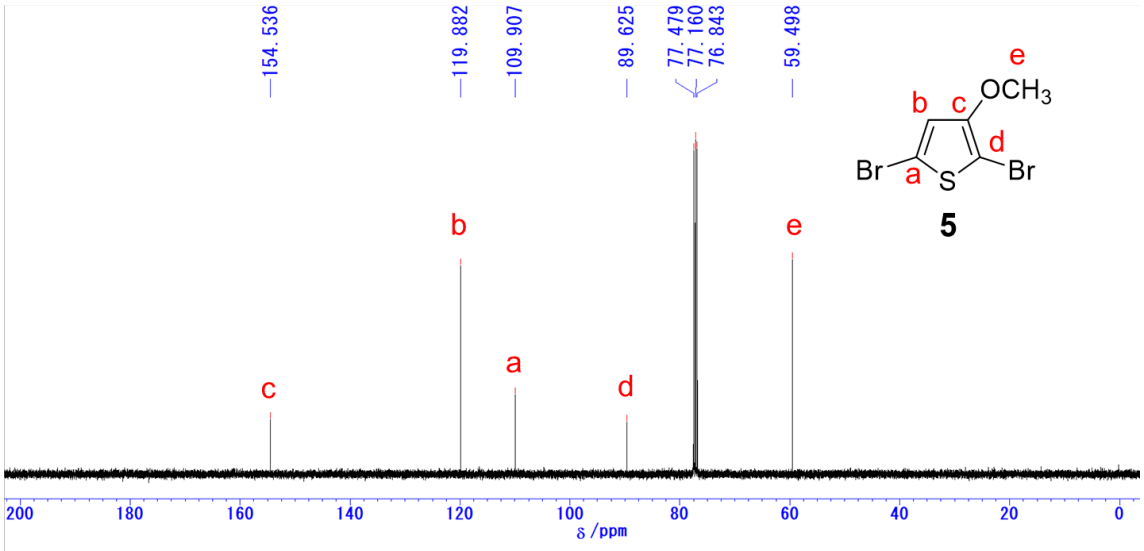


Figure S8 ^{13}C NMR spectrum of the 2,5-dibromo-3-methoxythiophene (**5**). (100 MHz, $CDCl_3$)

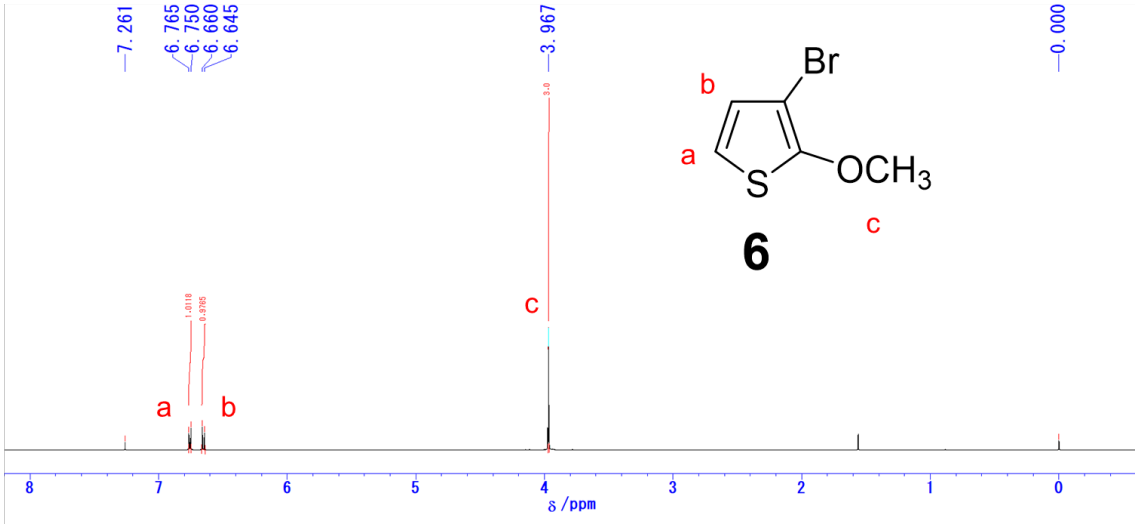


Figure S9 ^{1}H NMR spectrum of the 3-bromo-2-methoxythiophene (**6**). (400 MHz, $CDCl_3$)

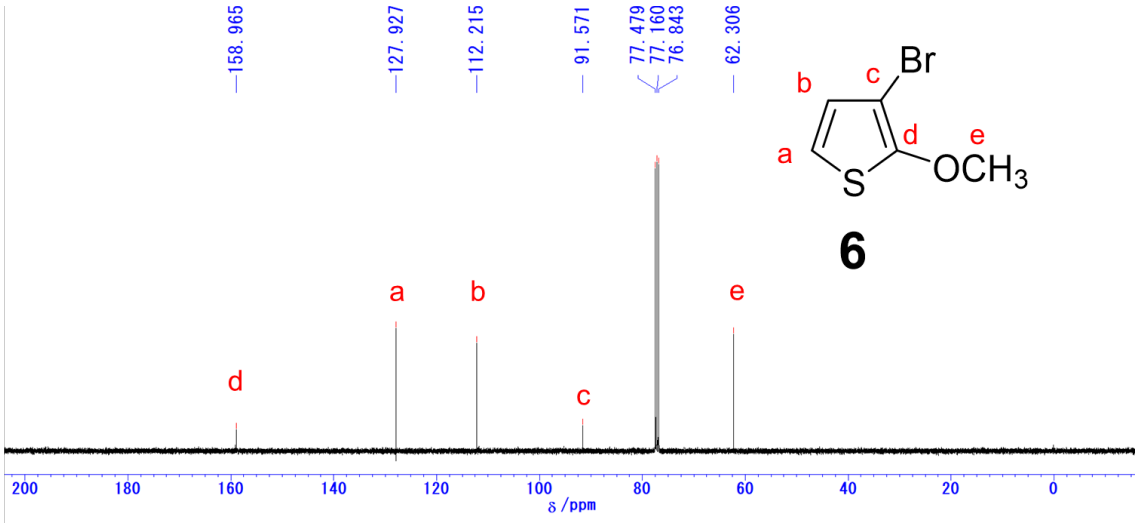


Figure S10 ^{13}C NMR spectrum of the 3-bromo-2-methoxythiophene (**6**). (100 MHz, $CDCl_3$)

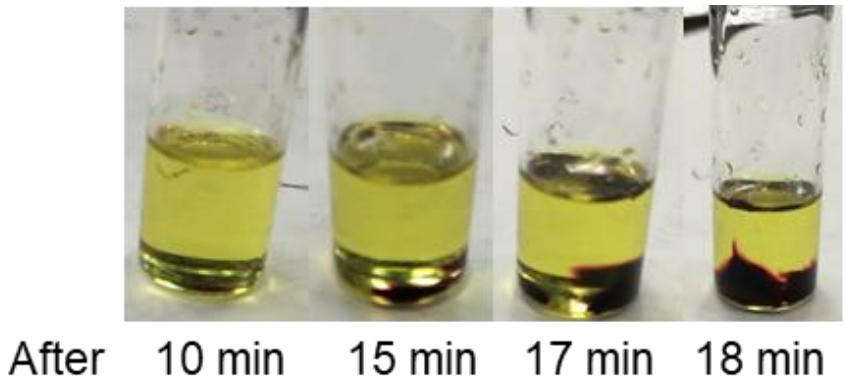


Figure S11 Generation and expansion of purple domain. The purple species was generated at the bottom of the container.

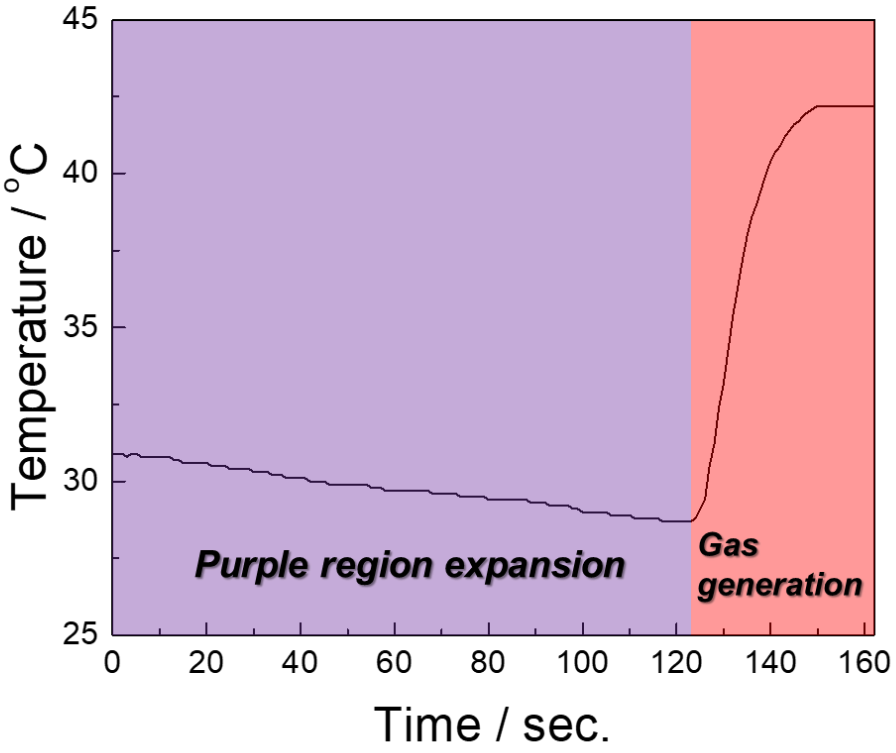


Figure S12 Temperature profile accompanied with proceeding of reaction. We monitored the temperature during expansion of purple region and gas generation. Initial proportional decreasing of temperature is air cooling after solvent evaporation using rotary evaporator. After gas generation, temperature was increased to 42.2 °C from 28.7 °C.

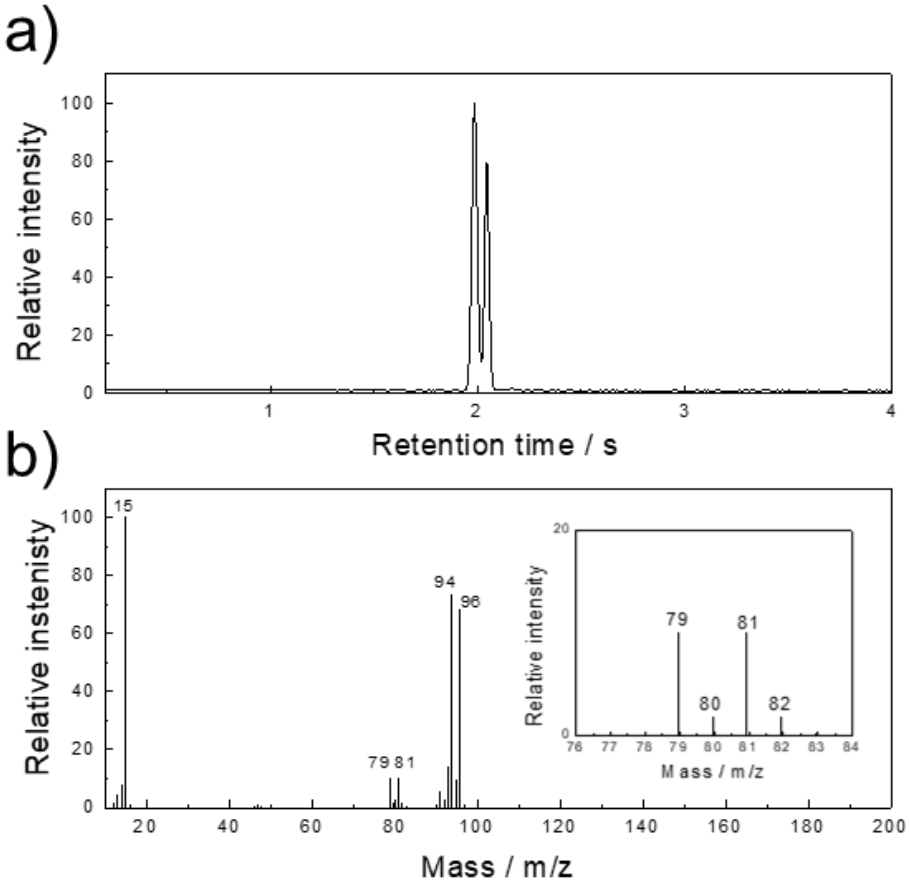


Figure S13 GC/MS spectra of brownish gas. a) Gas chromatogram and b) mass spectrum of the brownish gas. In the obtained two fractions in a), that obtained at 1.985 s was air, on the other hand, that obtained at 2.045 s was MeBr and HBr. b) The molecular ion peaks of M^+= 94 and 96 correspond to the mass of MeBr, and those of M^+= 80 and 82 in the inset correspond to that of HBr. Then, the peak intensity ratio of the MeBr and HBr was 1: 0.025.

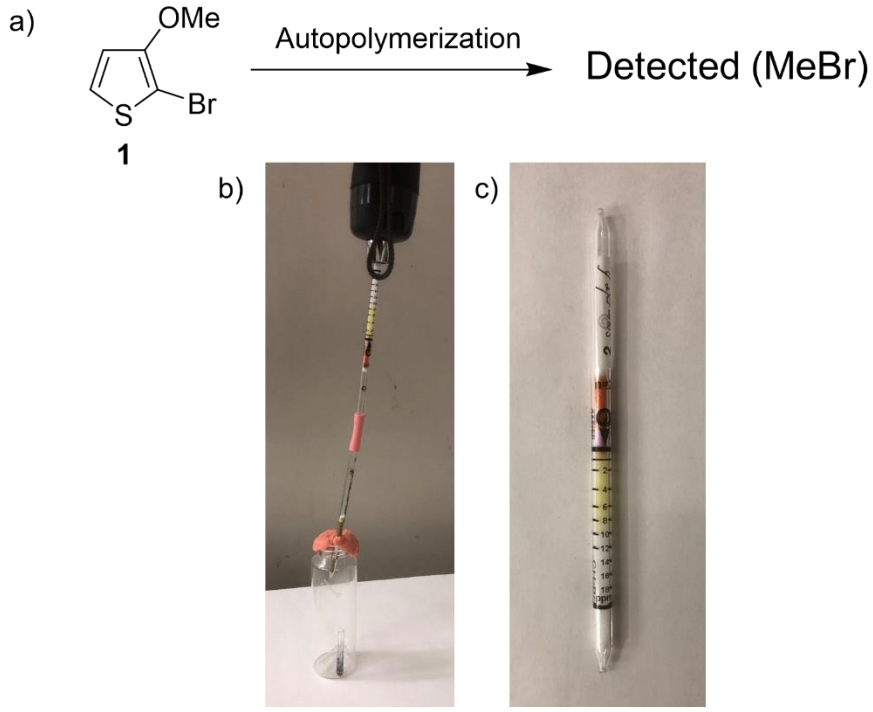


Figure S14 The photos of the setup of MeBr gas detection and gas detection tube.[S1)] a) Reaction scheme of this experiment. b) Setup of the gas detection (GASTECH GV-100S with No. 136LA detector tube for MeBr gas detection.). A microtube with 6.9 mg (3.6×10^{-5} mol) of pure compound **1** was put into the 100 mL sample tube, and we observed the autopolymerization in closed system. After the reaction, we covered the mouth of the sample tube with oil-based clay, and insert the detector tube. c) A result of the gas detection. This gas detector tube turns to yellow from white, if MeBr gas was detected. In this investigation, we sucked the gas twice with gas detector tube (No.136LA), then the scale of the tube showed 10 ppm. Generally, when using this detector tube, the basic number of suctions is 2 times. Therefore, this result indicated that the concentration of the MeBr gas is 10 ppm.

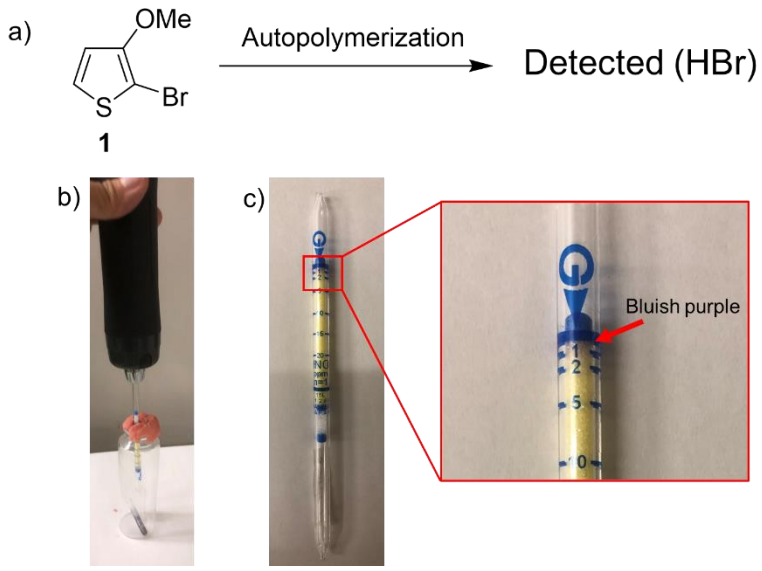


Figure S15 The photos of the setup of HBr gas detection and gas detection tube.[S1] a) Reaction scheme of this experiment. b) Setup of the gas detection (GASTECH GV-100S with No. 15L detector tube for HBr gas detection.). A microtube with 10.1 mg (5.2×10^{-5} mol) of pure compound **1** was put into the 100 mL sample tube, and we observed the autopolymerization in closed system. After the reaction, we covered the mouth of the sample tube with oil-based clay, and insert the detector tube. c) A result of the gas detection. This gas detector tube turns to bluish purple from yellow, if HBr gas was detected. In this investigation, we sucked the gas twice with gas detector tube (No.15L), then the scale of the tube showed 1 ppm. Generally, when using this detector tube, the basic number of suctions is once. Therefore, we multiplied 0.5 to the scale. In addition, we needed to multiply the coefficient depends on the kind of gases. In the case of the HBr gas, it needed to multiply 0.8 to the observed concentration. From the calculation, the concentration of the HBr gas was 0.4 ppm.

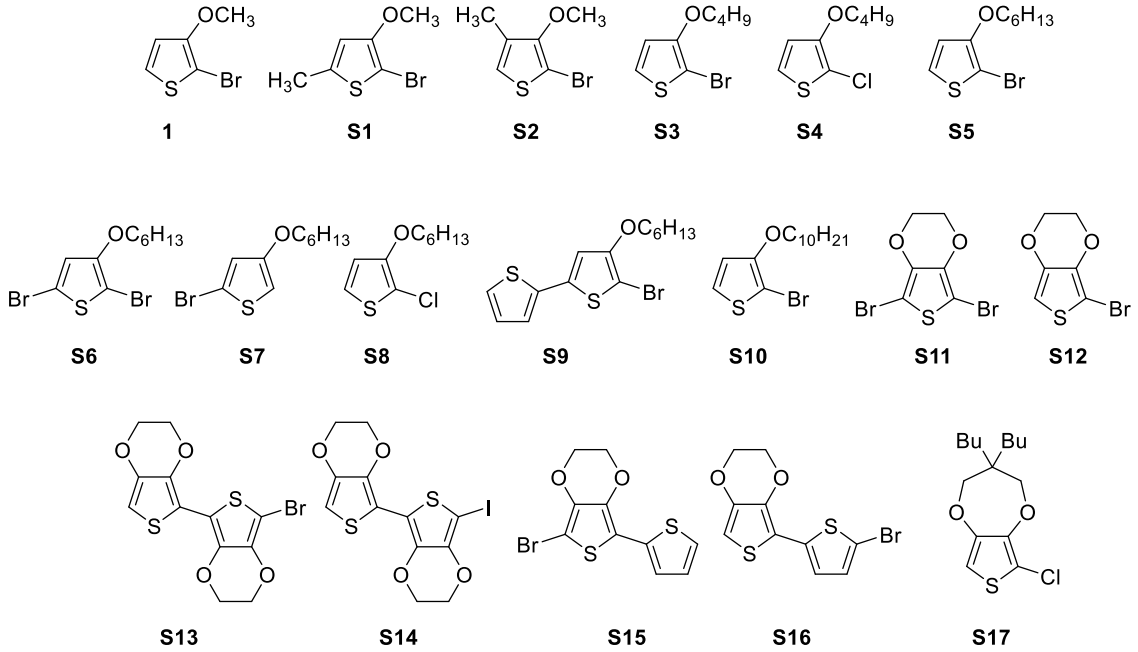
Table S1 Numerical conditions and results of gas detection by gas detection tube.

Gas	Amount of **1** (mg)	Detected concentration (ppm)	Calcd gas amount (mol)	Detection yield (%)
HBr	10.1 (5.2×10^{-5} mol)	0.4 (×2)	1.6×10^{-9}	3.1×10^{-3}
MeBr	6.9 (3.6×10^{-5} mol)	10 (×1)	4.1×10^{-8}	0.11

From the gas detection studies, we calculated the generation ratio of each gas content. We calculated the amount of the gas from the detected concentration. By using the amount of compound **1** and calculated gas amount, we estimated the yield of gas generation reaction as detection yield. Where, detection yield was calculated by the (amount of **1** (mol) / calculated gas amount (mol)) ×100. Then, we calculated the generation ratio of the MeBr and HBr gas from the ratio of the detection yield. The ratio of the detection yield of MeBr and HBr was 1: 0.028. This ratio shows good agreement with the result of the GC-MS analysis of the brownish gas (Fig. S13).

Figure S16 Photo of black residue. The black residue has metallic lustre.

Scheme S1 Molecular structures of alkoxythiophene derivatives, which were examined for (self-) acid assisted polycondensation ((S)AAP) reactivity.[S2-5)]



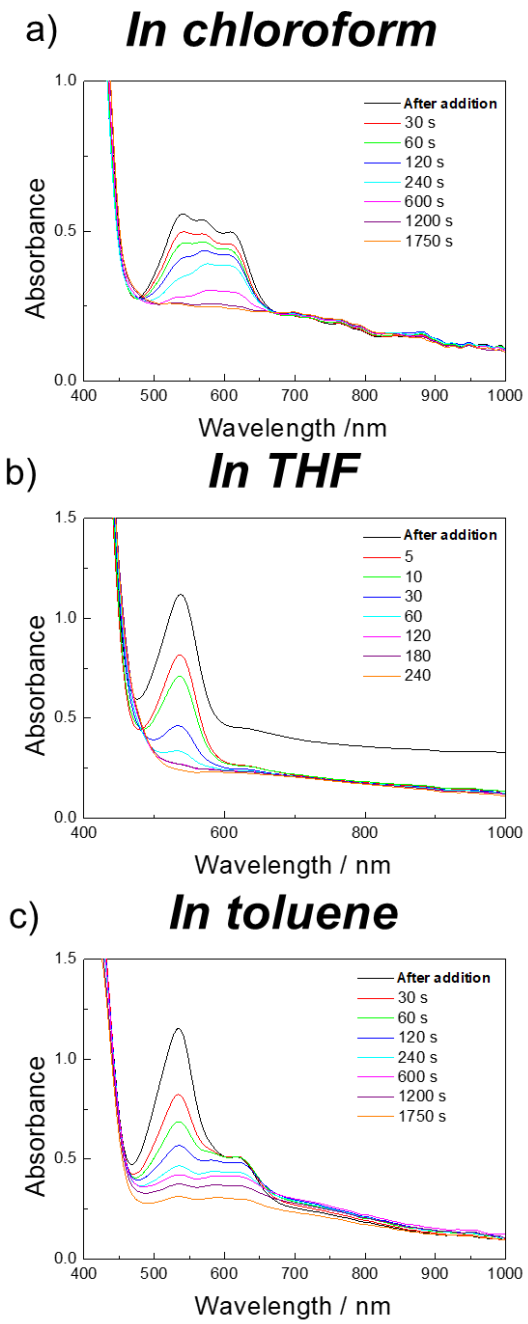


Figure S17 Absorption spectra transition of the purple liquid in the organic solvents. a) Absorption spectrum changes in chloroform, b) THF and c) toluene. In three typical organic solvents, the absorption band at near 600 nm were decreased with increasing the observation time.

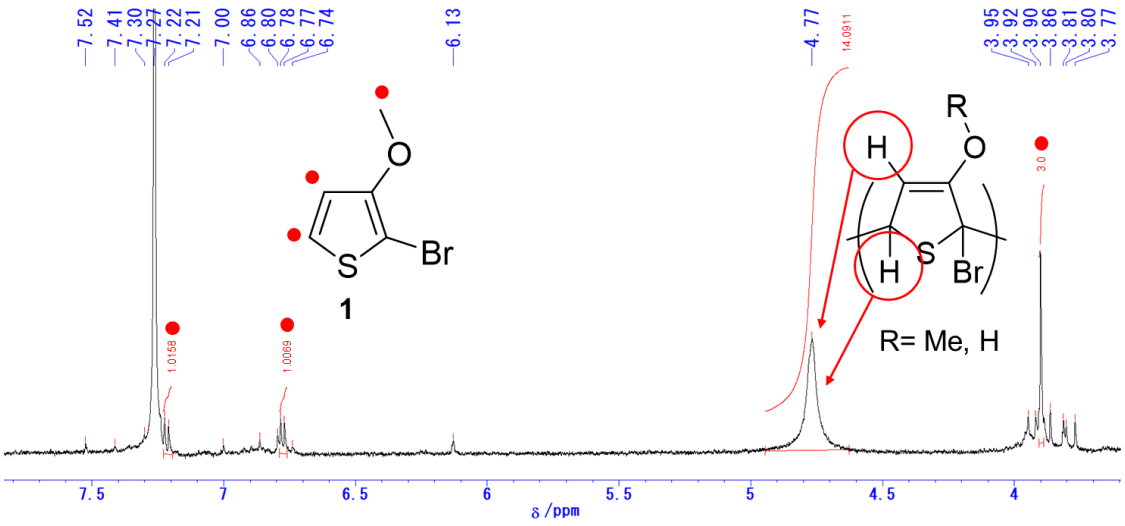


Figure S18 ^{1}H NMR spectrum of purple liquid quenched by $CDCl_3$. We added the $CDCl_3$ to the purple liquid to quench the reaction, and measured it. The signals marked with red dots are the signals of unreacted compound **1**. The other signals are newly generated oligomer's signals.

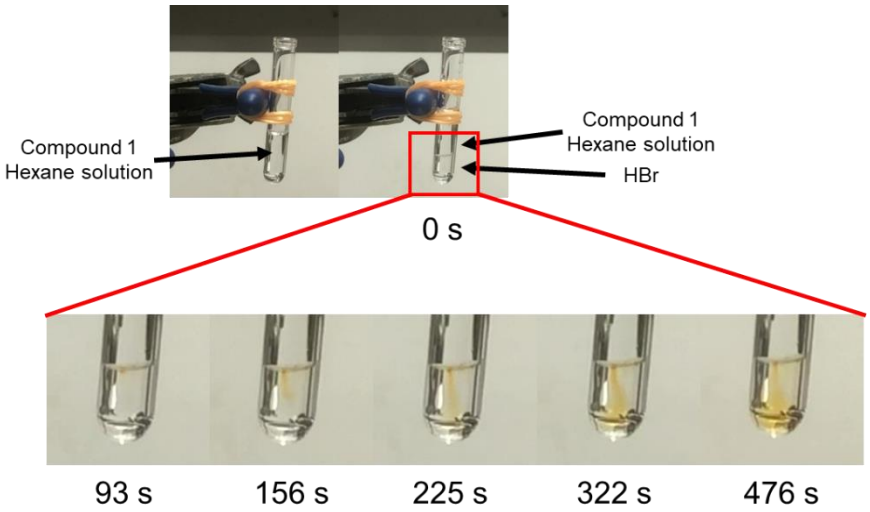


Figure S19 Photos of the reaction of the autopolymerization by adding the HBr to the hexane solution of compound **1**. The purple dot was generated at the interface between the hexane solution and HBr aqueous solution in the around 90 s after added the HBr aqueous solution to the hexacne solution.

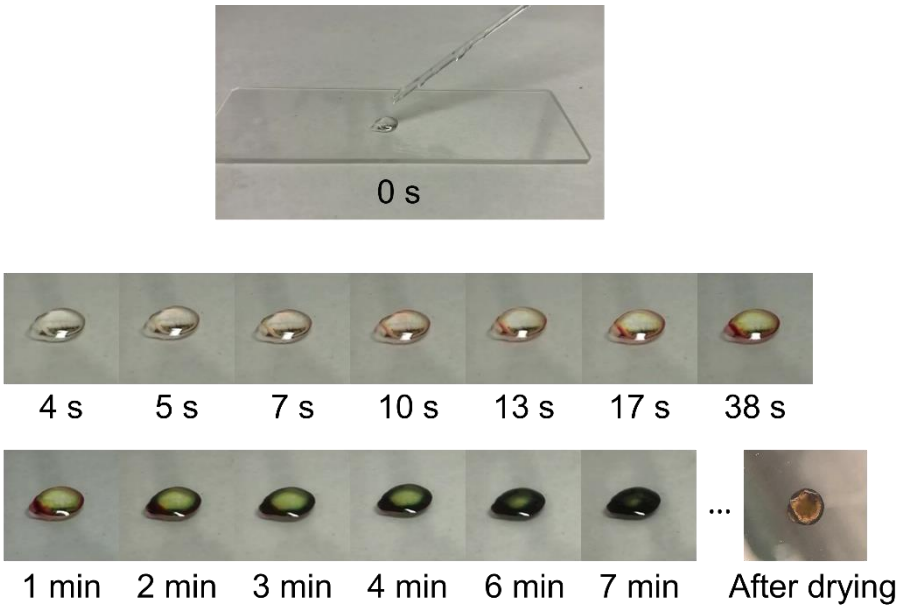


Figure S20 Photos of the reaction of the autopolymerization by adding the HBr to the pure compound **1**. By adding the HBr aqueous solution to the pure compound **1**, the purple region was appeared immediatery at the interface between the HBr aqueous solution and pure conpound **1**.

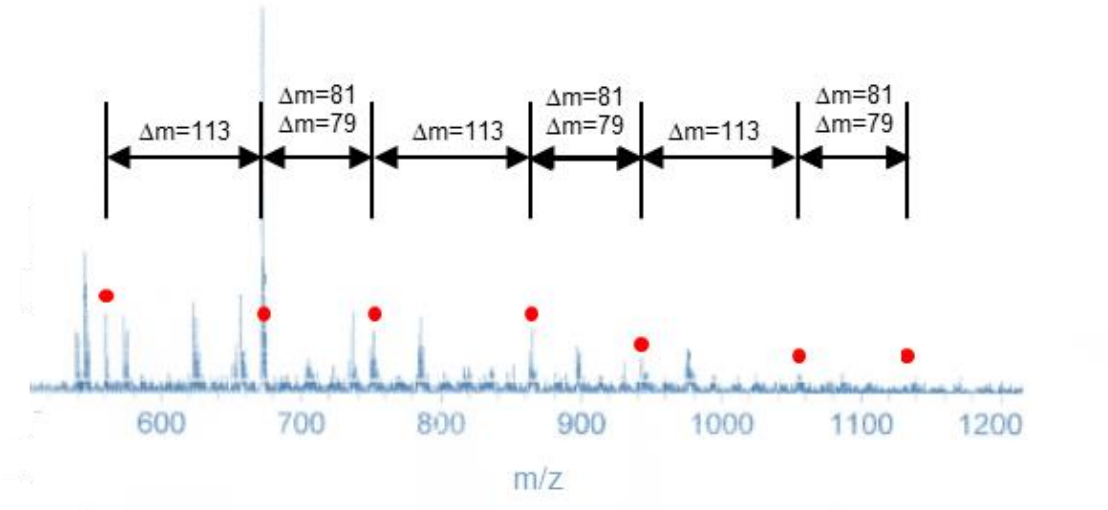


Figure S21 MALDI-TOF MS spectrum of methanol extract of black residue. The mass difference of 113 is **Monomer unit A**, which was bromine atom desorbed, and 79 and 81 is bromine atom.

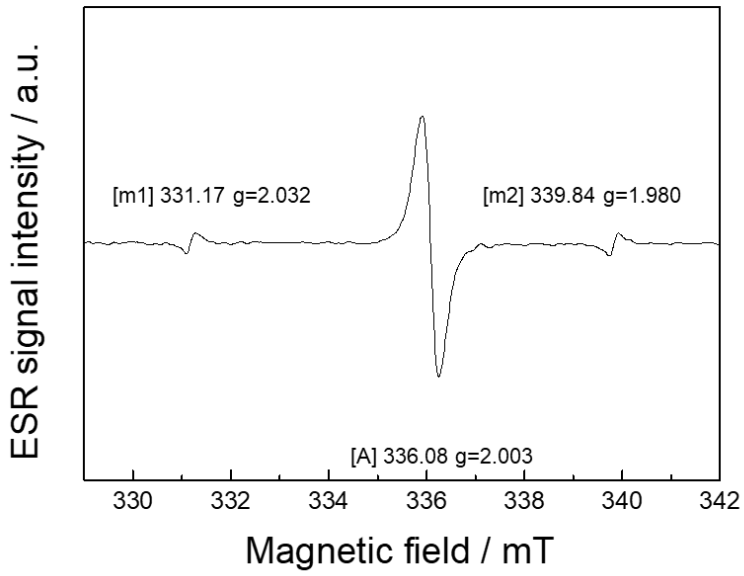


Figure S22 ESR spectrum of *n*-hexane extract of black residue. The sample was cooled for 30 min at -30 °C under nitrogen atmosphere.

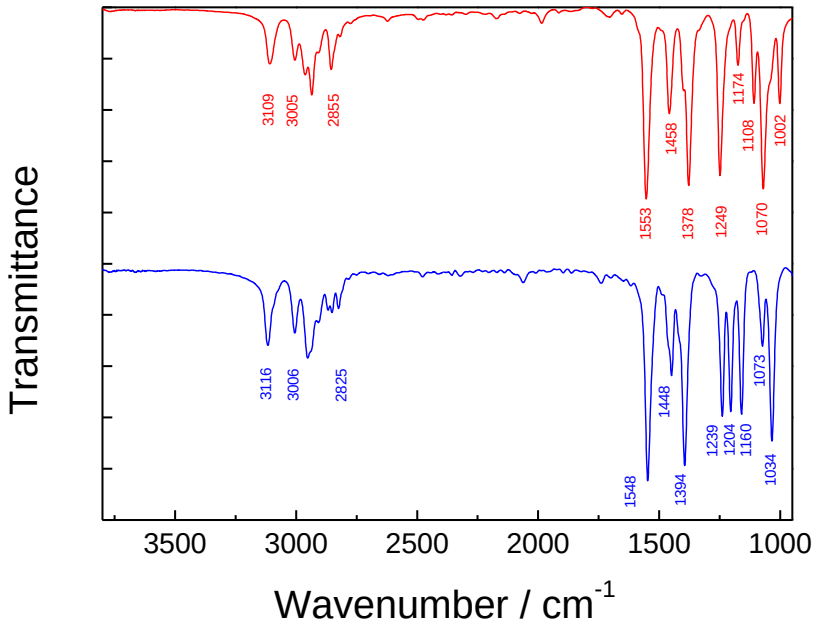


Figure S23 FT-IR spectrum of compound **1** and **4**. The red solid line shows FT-IR spectrum of compound **1**, and blue solid line shows that of compound **4**.

Table S2 Detailed infrared band assignment of compound **1** and **4** associated with Fig. S23.

Vibration	Compound **1** (cm^{-1})	Compound **4** (cm^{-1})
C=C－H stretch	3109	3116
C－C－H stretch	3005-2855	3006-2825
C=C stretch	1553	1548
－CH_3 bend	1458, 1378	1448, 1394
C_β－H in-plane bend	1070	1034
C－Br stretch	1002	－

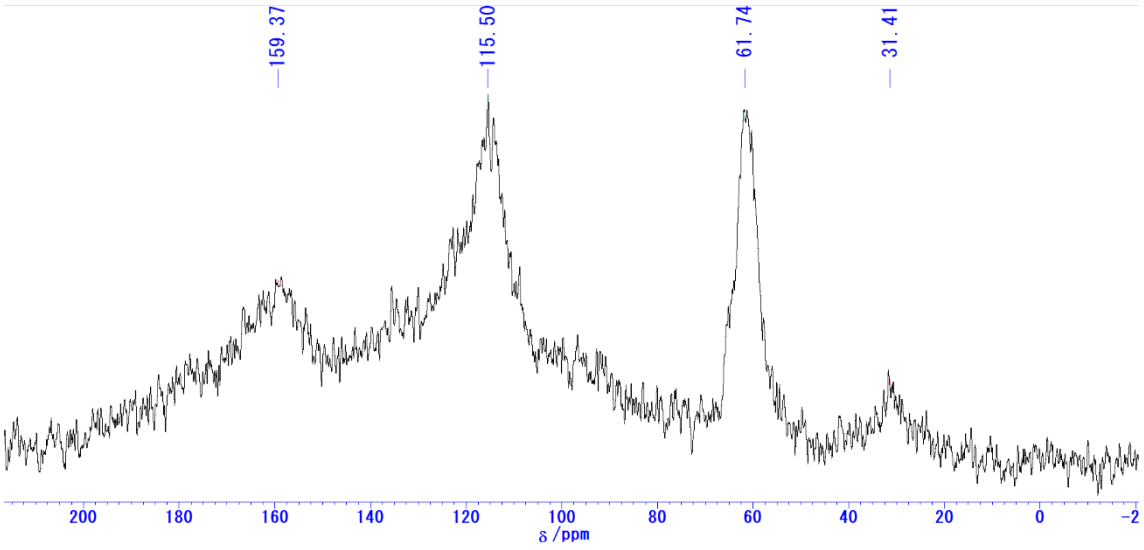
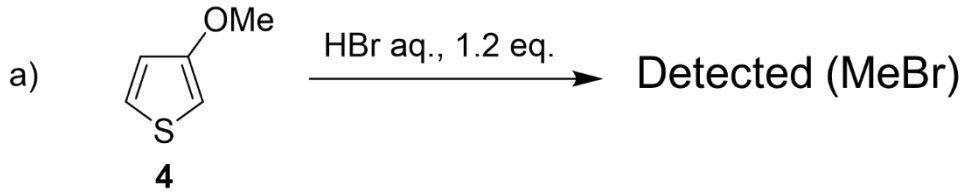


Figure S24. Solid-state ^{13}C NMR spectrum of the black residue. (100 MHz)



b)

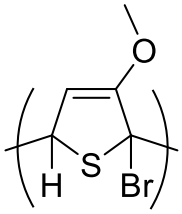
Figure S25 The photo of a gas detection tube for detection of HBr. a) Reaction scheme of this experiment. b) A result of the gas detection. A microtube with 19.8 mg (1.7×10^{-4} mol) of pure compound **4** and 35.9 mg (2.1×10^{-4} mol) of hydrobromic acid (49%) was put into the 1000 mL beaker overnight in closed system. After the reaction, we covered the mouth of the beaker with oil-based clay and glass plate, and insert the detector tube. This gas detector tube turns to bluish purple from yellow, if HBr gas was detected. In this investigation, we sucked the gas with gas detector tube (No.136LA) in once, the scale of the tube showed 18 ppm. Generally, when using this detector tube, the basic number of suctions is twice. Therefore, we multiplied 2 to the scale. From the calculation, the concentration of the MeBr gas was 34 ppm.

Table S3 Numerical conditions and results of the reaction of compound **4** and HBr aqueous.

Gas	Amount of **1** (mg)	Amount of HBr aq. (mg)	Detected concentration (ppm)	Calcd gas amount (mol)	Detection yield (%)
MeBr	19.8 (1.7×10^{-4} mol)	35.9 (2.1×10^{-4} mol)	34 (×1/2)	1.7×10^{-6}	1.0

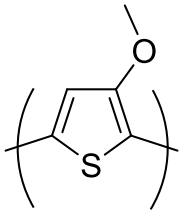
Table S4 Numerical calculation of the ratio of each monomer unit in polymer.

Elements	C	H	O	Br	S
Molar mass (g/mol)	12.01	1.008	16.0	79.9	32.07
Found %	34.71	2.55	11.21	30.21	20.3
Found / Molar mass	2.890	2.53	0.701	0.378	0.633
Ratio based on S	4.57	4.00	1.11	0.60	1



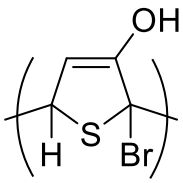
Monomer Unit A

C_5H_5OBrS



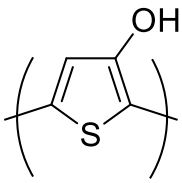
Monomer Unit B

C_5H_4OS



Monomer Unit A'

C_4H_3OBrS



Monomer Unit B'

C_4H_2OS

From the calculated ratio of carbon atom (4.57) based on the ratio of sulfur atom (Table 1), the progression of the demethylation reactions was about 43%. The close progression values of the reaction steps 2 and 3 is roughly consistent with the fact that most of the observed gas components were methyl bromide (MeBr: HBr = 1: 0.025). Assuming that the progressions of the reaction steps 2 and 3 were actually 0.4, the approximate ratio of monomer unit is [A]: [B]: [A′]: [B′] = R_a: 0.6−R_a: 0.6−R_a: −0.2+R_a, where R_a = [A] / ([A]+[B]+[A′]+[B′]) and 0.2 < R_a <0.6. Excess ratios of hydrogen (0.20) and oxygen (0.11) atoms based on the ratio of sulfur atom can be explained by the absorption of about 10% water by the polyhydroxy polymer.

References

1) R. Kodama, K. Sumaru, K. Morishita, T. Kanamori, K. Hyodo, T. Kamitanaka, M. Morimoto, S. Yokojima, S. Nakamura, K. Uchida, *Chem. Commun.* **2015**, *51*, 1736–1738.
2) P. Wagner, K. W. Jolley, D. L. Officer, *Aust. J. Chem.* **2011**, *64*, 335–338.
3) Y. Yin, Z. Li, J. Jin, C. Tusy, J. Xia, *Synth. Met.* **2013**, *175*, 97–102.
4) A. Balasubramanian, T.-C. Ku, H.-P. Shih, A. Suman, H.-J. Lin, T.-W. Shih, C.-C. Han, *Polym. Chem.* **2014**, *5*, 5928–5941.
5) C. Tusy, K. Jiang, K. Peng, L. Huang, J. Xia, *Polym. Chem.* **2015**, *6*, 1014–1022.