

Supporting Information

Organic ionic plastic crystals composed of tetrahydrothiophenium cation with high conductivity

Keita Inoue, Yoshifumi Hirotsu, Yuko Takeoka, Masahiro Rikukawa,

Masahiro Yoshizawa-Fujita*

Department of Materials & Life Sciences, Sophia University

7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan

E-mail: masahi-f@sophia.ac.jp

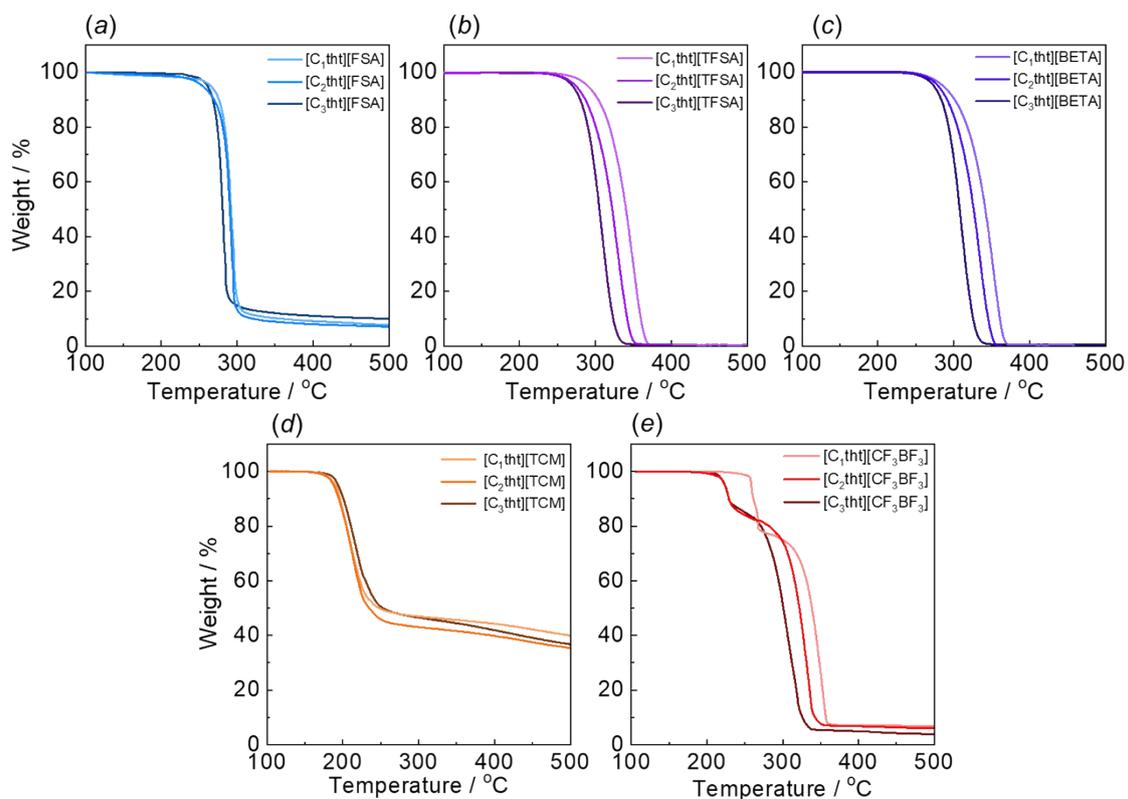


Figure S1. TG curves of tetrahydrothiophenium salts. a) $[C_n\text{tht}][\text{FSA}]$, b) $[C_n\text{tht}][\text{TFSA}]$, c) $[C_n\text{tht}][\text{BETA}]$, d) $[C_n\text{tht}][\text{TCM}]$, e) $[C_n\text{tht}][\text{CF}_3\text{BF}_3]$ ($n = 1, 2, \text{ and } 3$).

Table S1. Ionic conductivity of tetrahydrothiophenium salts at 25°C.

sample	$\sigma / \text{S cm}^{-1}$
[C ₁ tht][TFSA]	6.59×10^{-9}
[C ₂ tht][TFSA]	2.54×10^{-7}
[C ₃ tht][TFSA]	7.18×10^{-7}
[C ₁ tht][BETA]	2.80×10^{-6}
[C ₂ tht][BETA]	9.86×10^{-8}
[C ₃ tht][BETA]	4.04×10^{-4}
[C ₁ tht][FSA]	1.50×10^{-7}
[C ₂ tht][FSA]	2.07×10^{-5}
[C ₃ tht][FSA]	3.09×10^{-3}
[C ₁ tht][CF ₃ BF ₃]	3.39×10^{-7}
[C ₂ tht][CF ₃ BF ₃]	7.19×10^{-4}
[C ₃ tht][CF ₃ BF ₃]	5.14×10^{-3}
[C ₁ tht][TCM]	2.00×10^{-5}
[C ₂ tht][TCM]	8.19×10^{-3}
[C ₃ tht][TCM]	6.45×10^{-7}

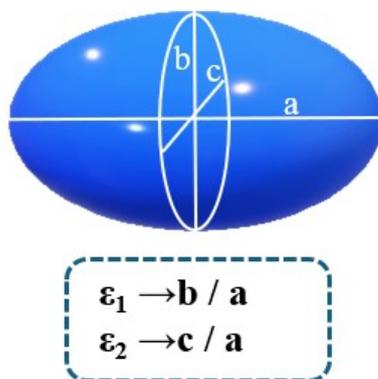


Figure S2. Schematic diagram of ellipticity parameters.

Table S2. □ Ion radius, ϵ_1 , and ϵ_2 of tetrahydrothiophenium salts.

Sample	Ion radius / Å	ϵ_1	ϵ_2
[C ₁ tht]	2.94	0.51	0.17
[C ₂ tht]	3.08	0.27	0.13
[C ₃ tht]	3.22	0.14	0.03
TFSA	3.34	0.16	0.12
BETA	3.68	0.12	0.10
FSA	2.87	0.24	0.23
CF ₃ BF ₃	2.68	0.48	0.46
TCM	2.68	0.95	9.14×10^{-6}

Table S3. Ion radius ratio of tetrahydrothiophenium salts.

Sample	Ion radius ratio
[C ₁ tht][TFSA]	0.88
[C ₂ tht][TFSA]	0.92
[C ₃ tht][TFSA]	0.96
[C ₁ tht][BETA]	0.80
[C ₂ tht][BETA]	0.84
[C ₃ tht][BETA]	0.87
[C ₁ tht][FSA]	0.98
[C ₂ tht][FSA]	0.93
[C ₃ tht][FSA]	0.89
[C ₁ tht][CF ₃ BF ₃]	0.91
[C ₂ tht][CF ₃ BF ₃]	0.86
[C ₃ tht][CF ₃ BF ₃]	0.83
[C ₁ tht][TCM]	0.91
[C ₂ tht][TCM]	0.87
[C ₃ tht][TCM]	0.83

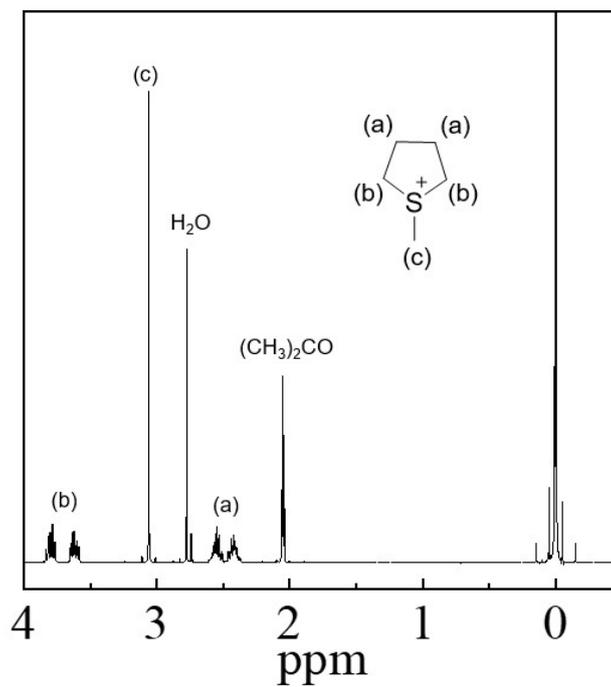


Figure S4. ^1H NMR spectrum of $[\text{C}_1\text{tht}][\text{FSA}]$ in $(\text{CD}_3)_2\text{CO}$.

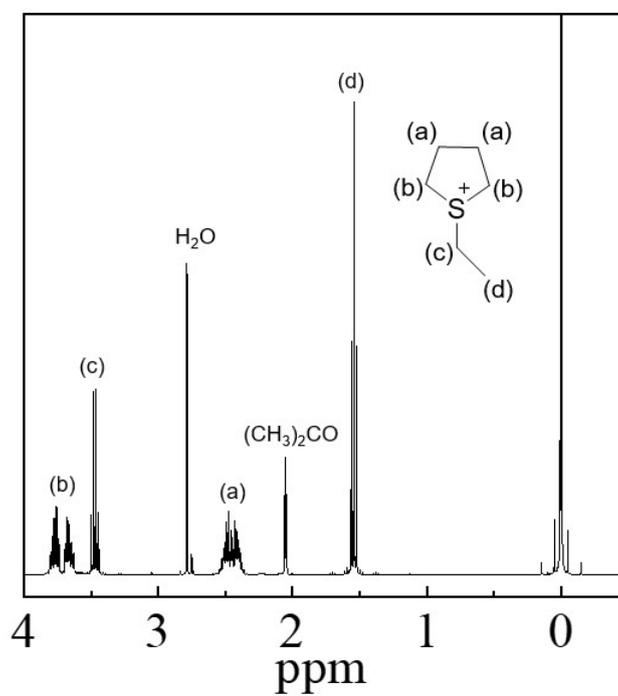


Figure S5. ^1H NMR spectrum of $[\text{C}_2\text{tht}][\text{FSA}]$ in $(\text{CD}_3)_2\text{CO}$.

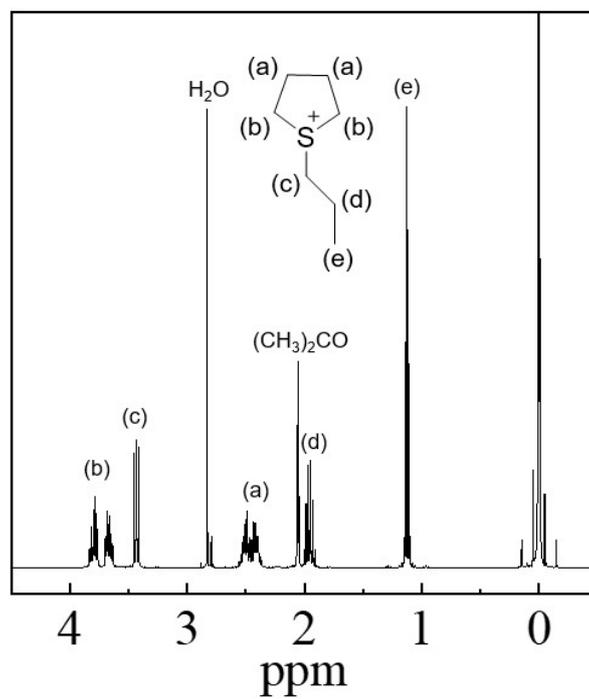


Figure S6. ^1H NMR spectrum of [C₃tht][FSA] in (CD₃)₂CO.

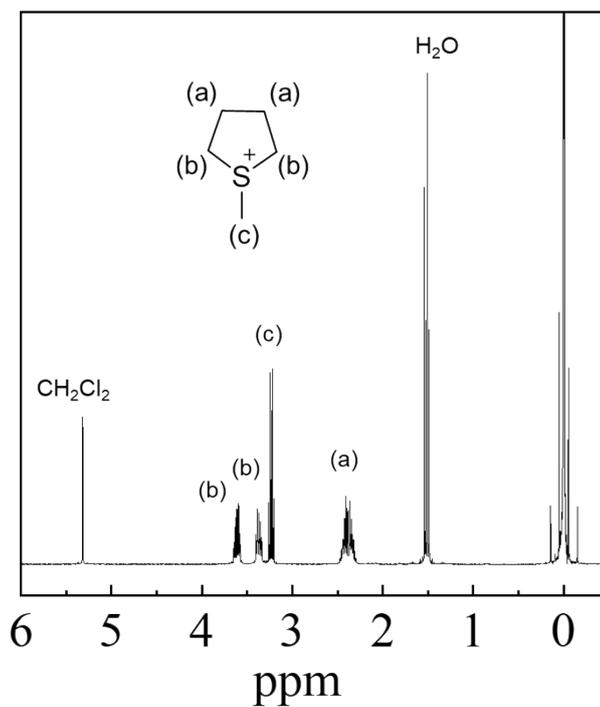


Figure S7. ^1H NMR spectrum of [C₁tht][TFSA] in (CD)₂Cl₂.

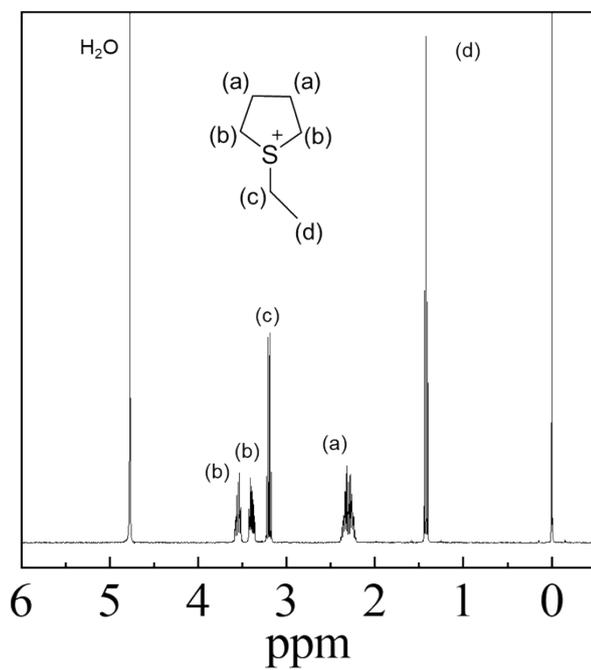


Figure S8. ¹H NMR spectrum of [C₂tht][TFSA] in D₂O.

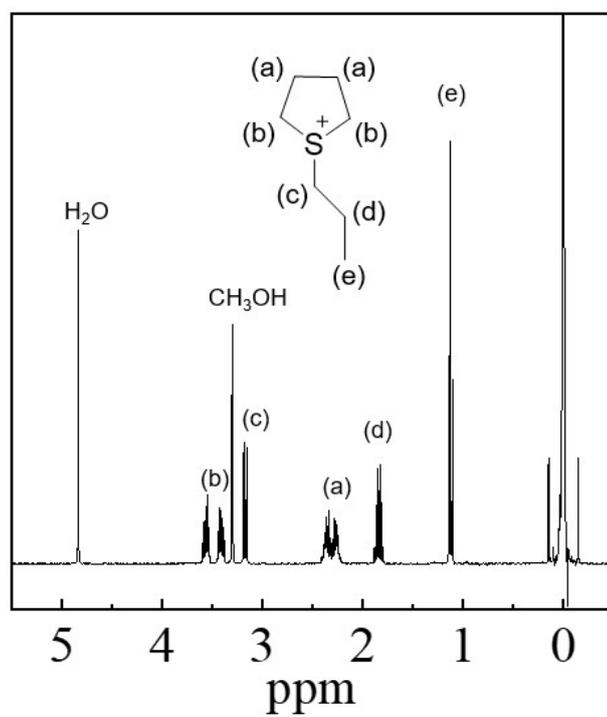


Figure S9. ¹H NMR spectrum of [C₃tht][TFSA] in CD₃OD.

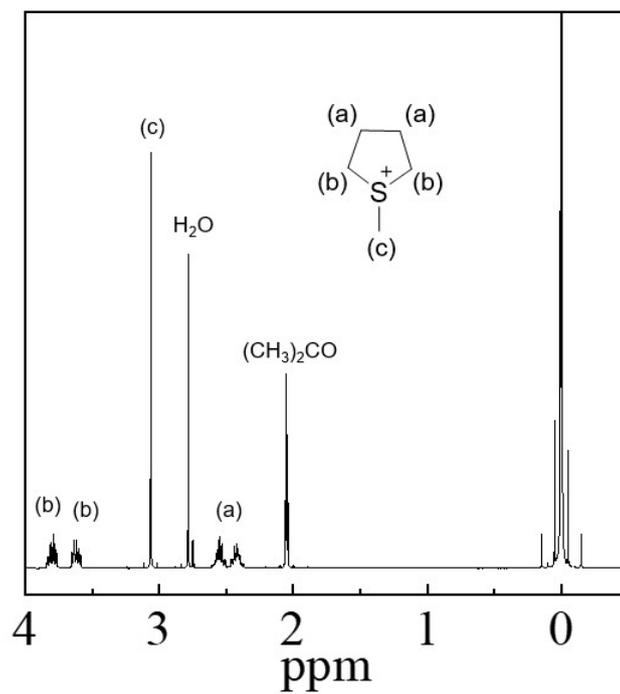


Figure S10. ¹H NMR spectrum of [C₁tht][BETA] in (CD₃)₂CO.

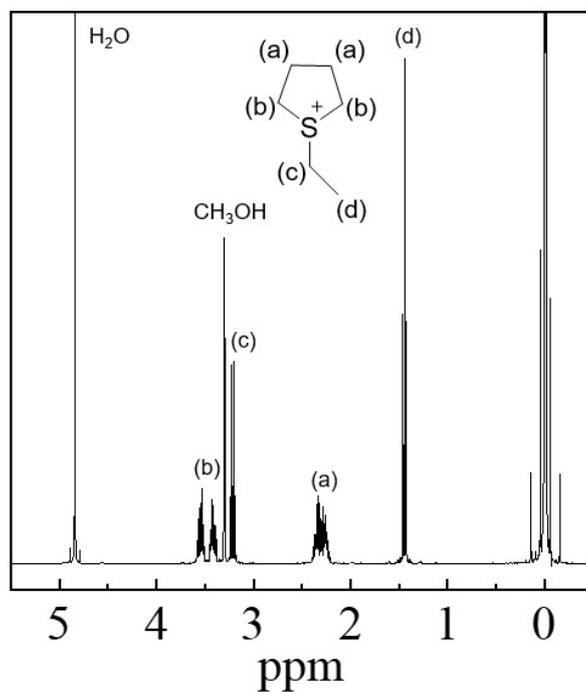


Figure S11. ¹H NMR spectrum of [C₂tht][BETA] in CD₃OH.

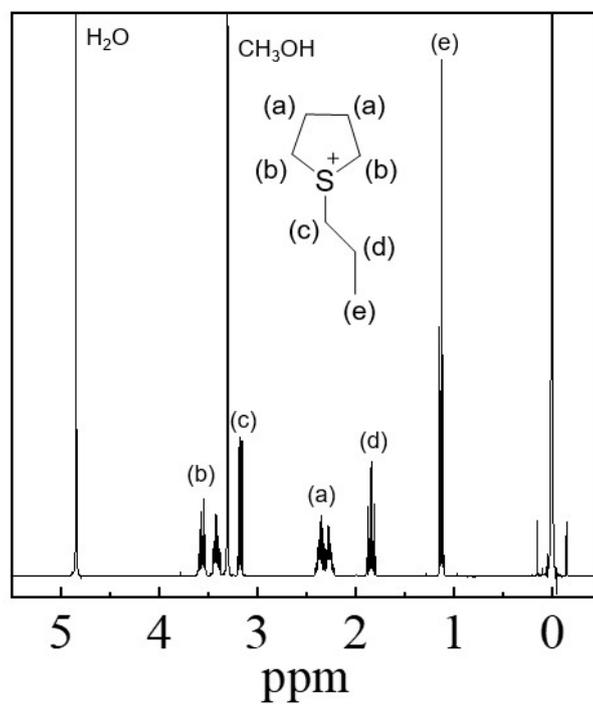


Figure S12. ^1H NMR spectrum of [C₃tht][BETA] in CD₃OD.

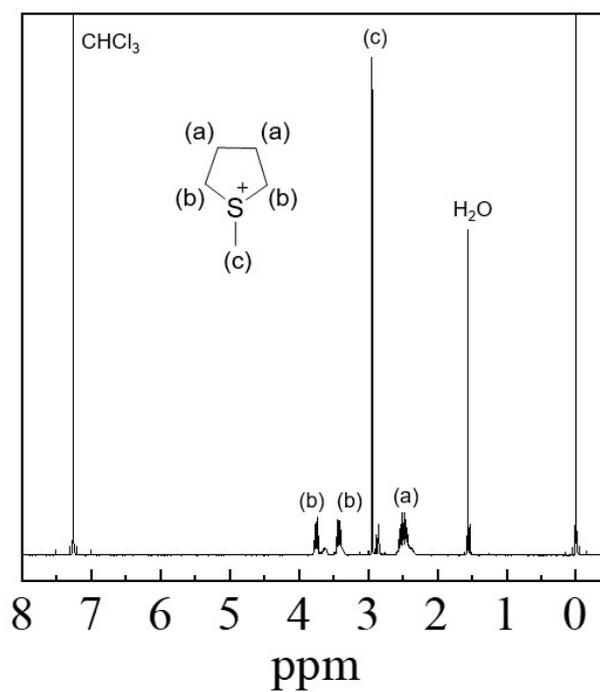


Figure S13. ^1H NMR spectrum of [C₁tht][TCM] in CDCl₃.

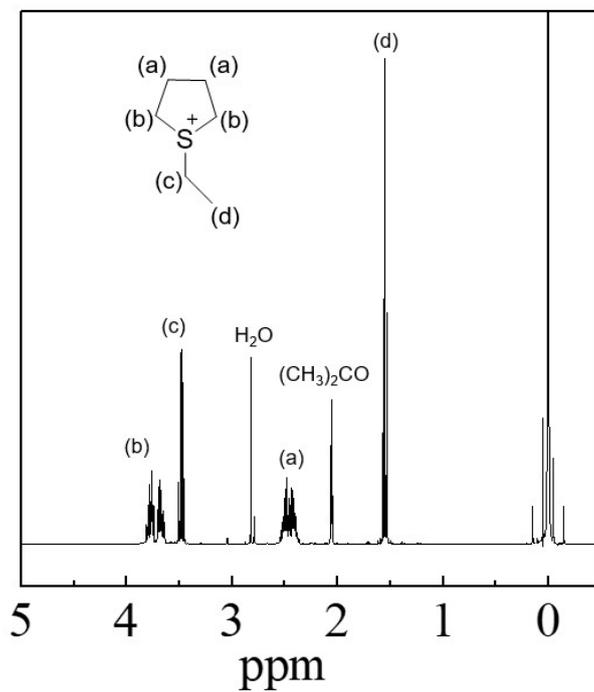


Figure S14. ¹H NMR spectrum of [C₂tht][TCM] in (CD₃)₂CO.

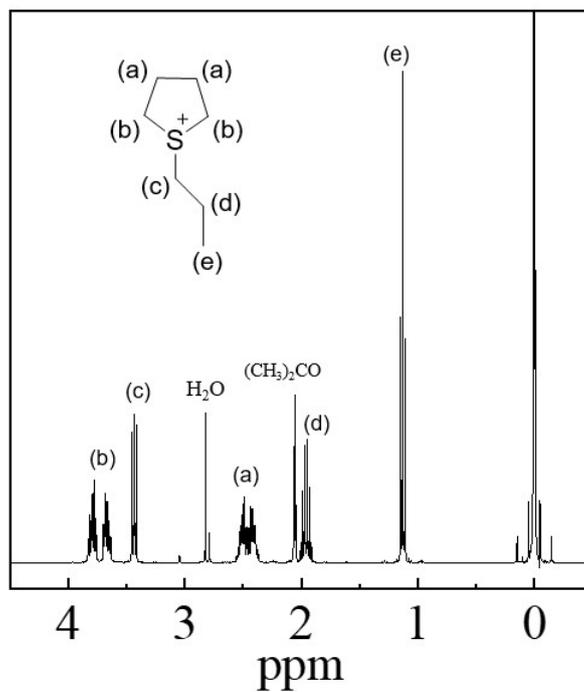


Figure S15. ¹H NMR spectrum of [C₃tht][TCM] in (CD₃)₂CO.

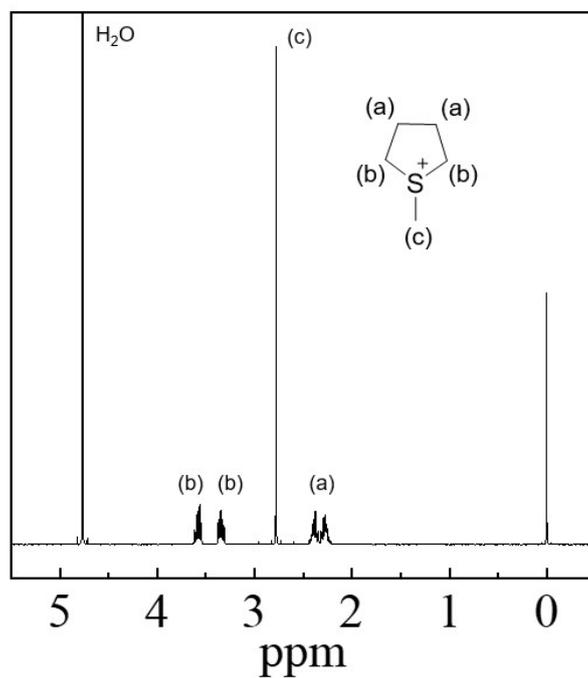


Figure S16. ^1H NMR spectrum of $[\text{C}_1\text{tth}][\text{CF}_3\text{BF}_3]$ in D_2O .

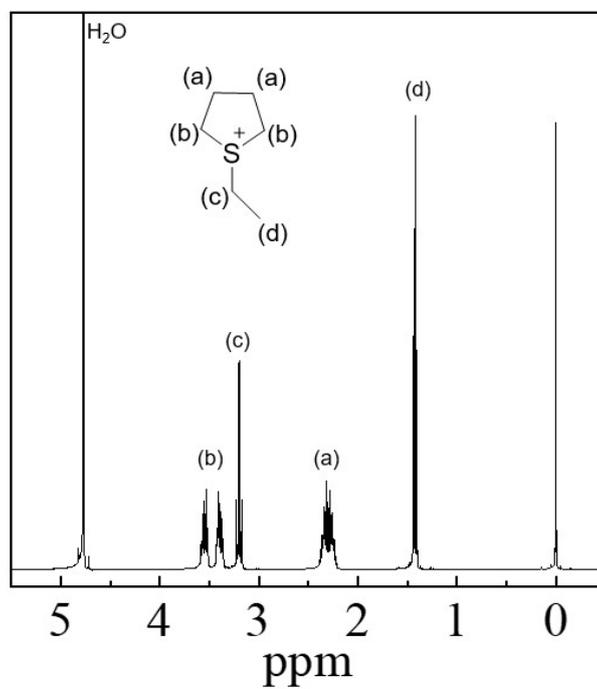


Figure S17. ^1H NMR spectrum of $[\text{C}_2\text{tth}][\text{CF}_3\text{BF}_3]$ in D_2O .

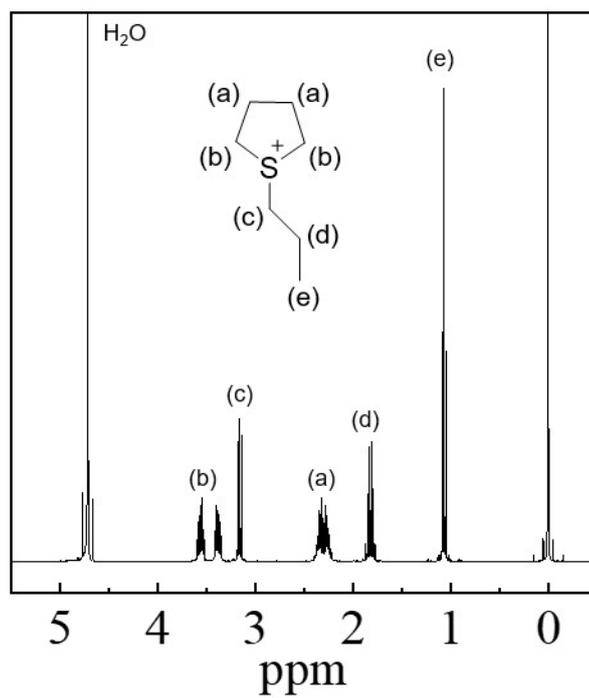


Figure S18. ^1H NMR spectrum of $[\text{C}_3\text{tht}][\text{CF}_3\text{BF}_3]$ in D_2O .