Supporting Information Materials

for

Benzenedithiolate-bridged MoFe complexes: structures, oxidation states, and reactivities

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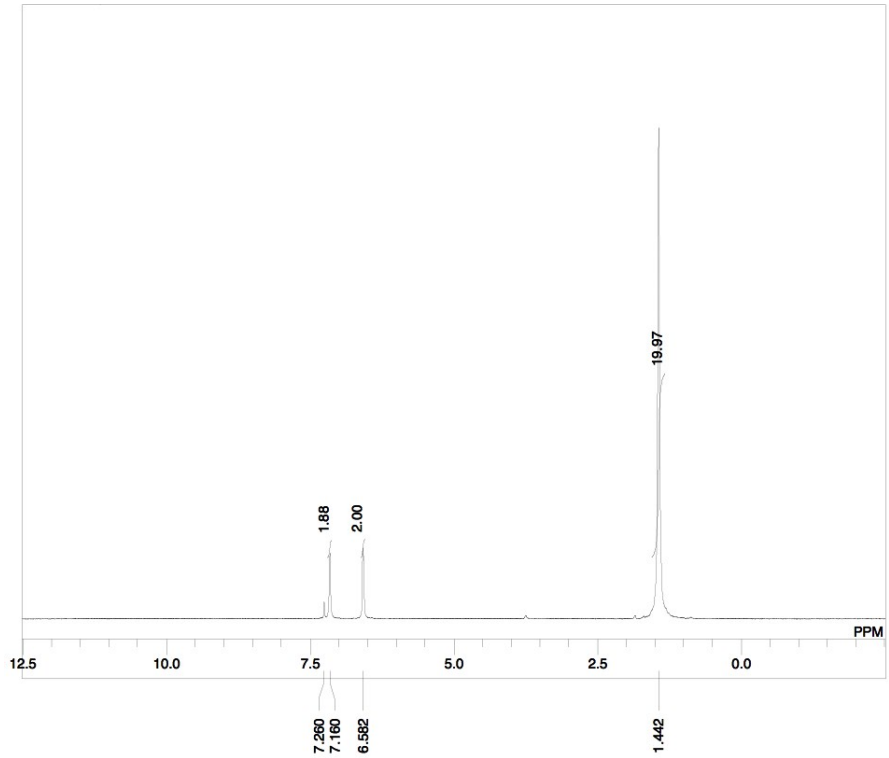

Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$.

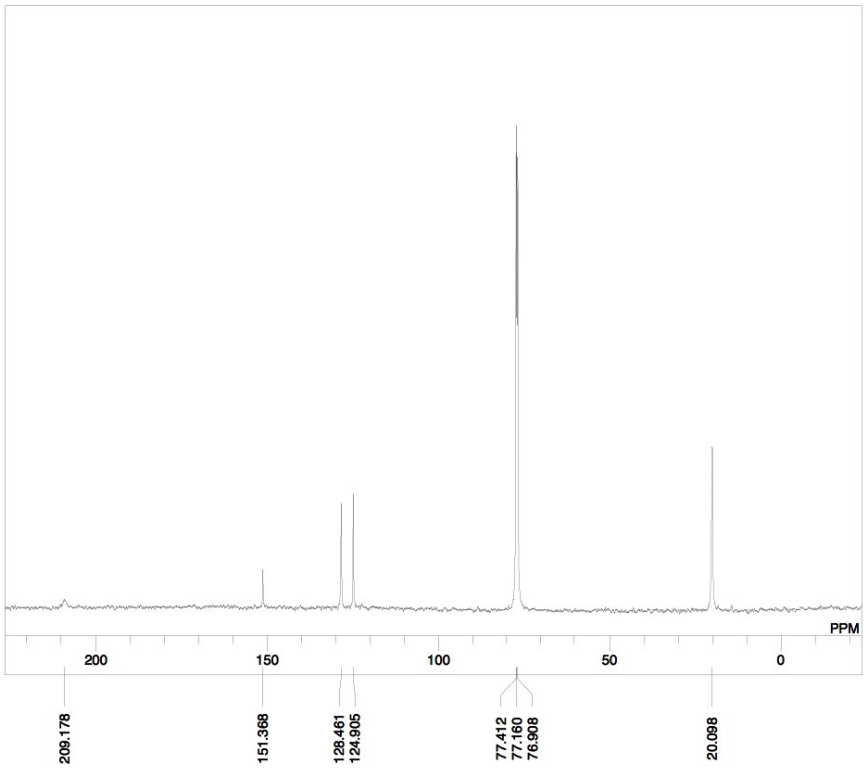

Figure S2. ^{13}C NMR spectrum of **1** in $CDCl_3$.

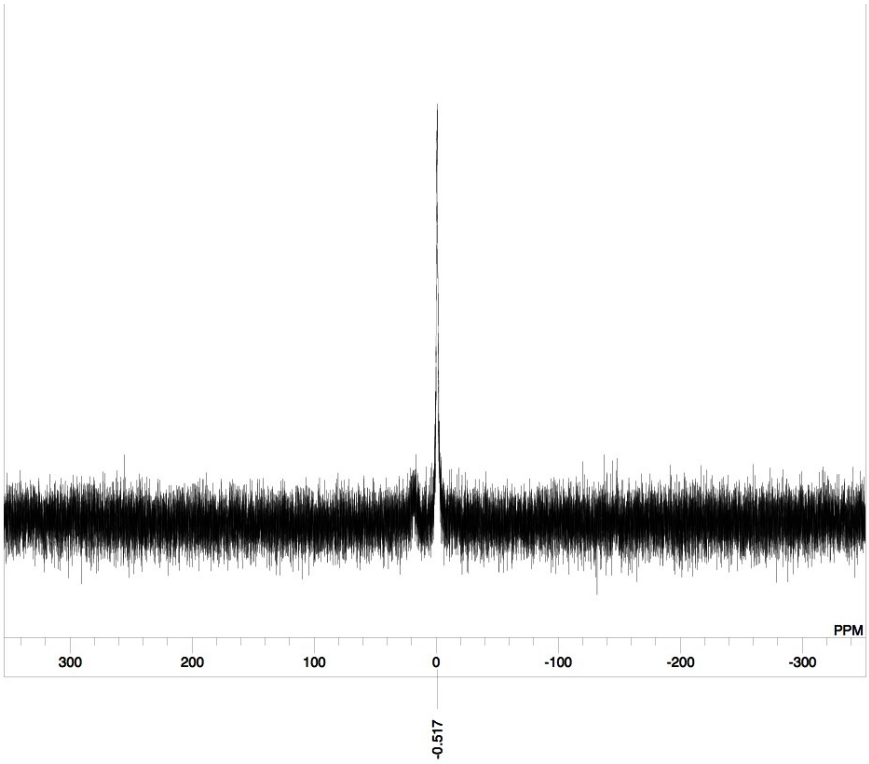

Figure S3. ^{31}P NMR spectrum of **1** in $CDCl_3$.

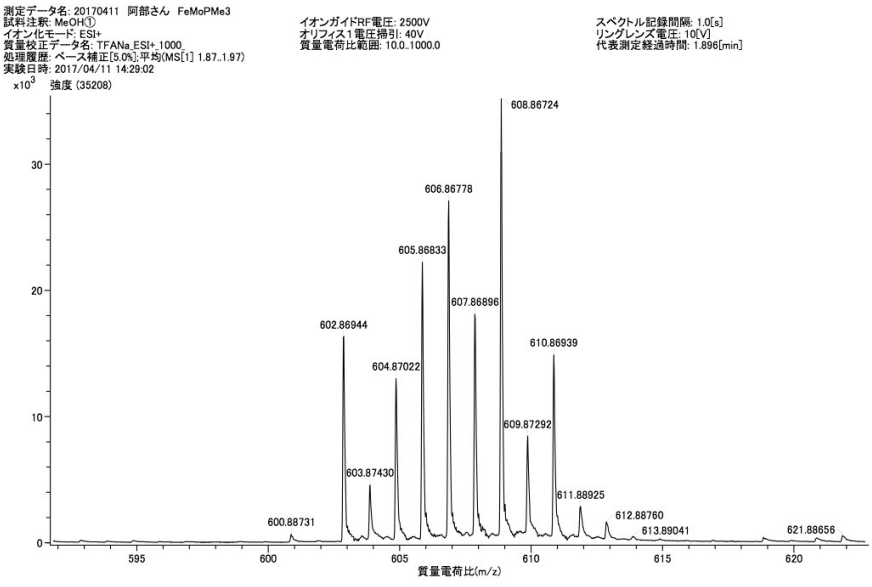

Figure S4. High resolution mass spectrum (ESI-TOF, positive) of **1**.

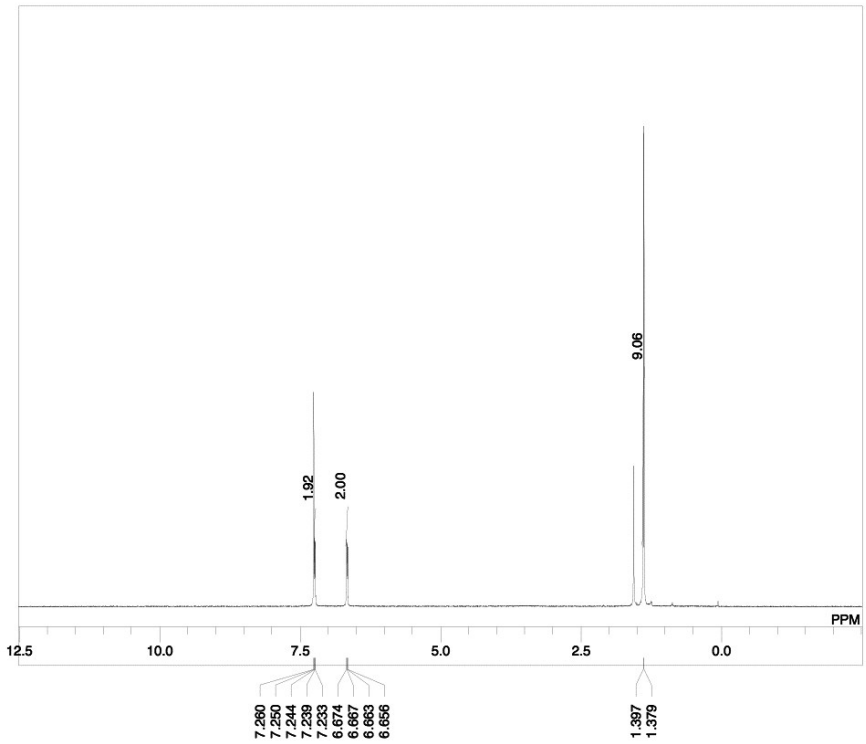

Figure S5. ^{1}H NMR spectrum of **2** in $CDCl_3$.

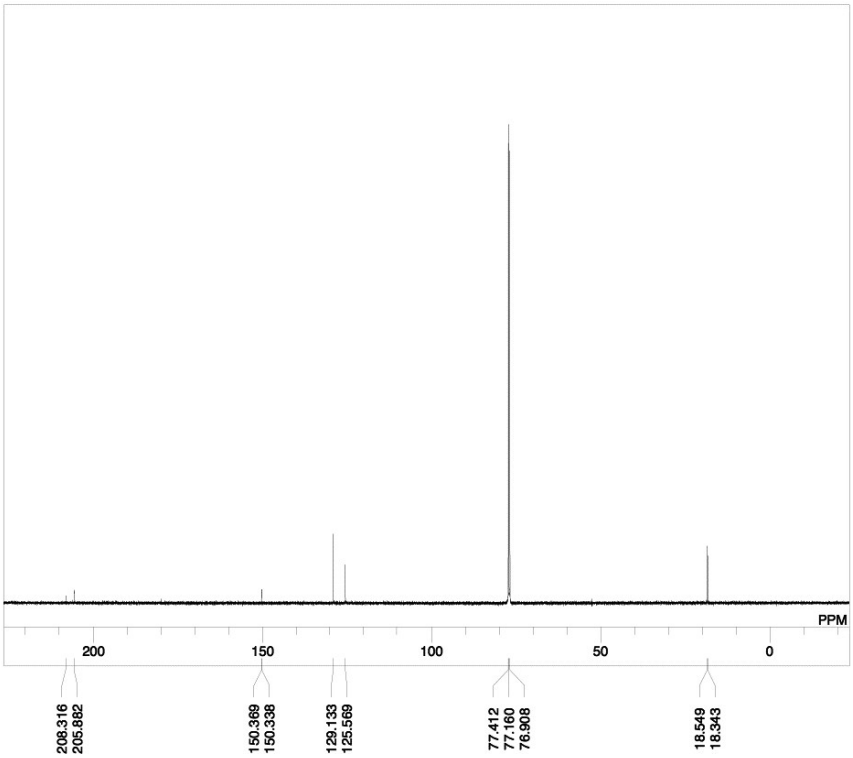

Figure S6. ^{13}C NMR spectrum of **2** in $CDCl_3$.

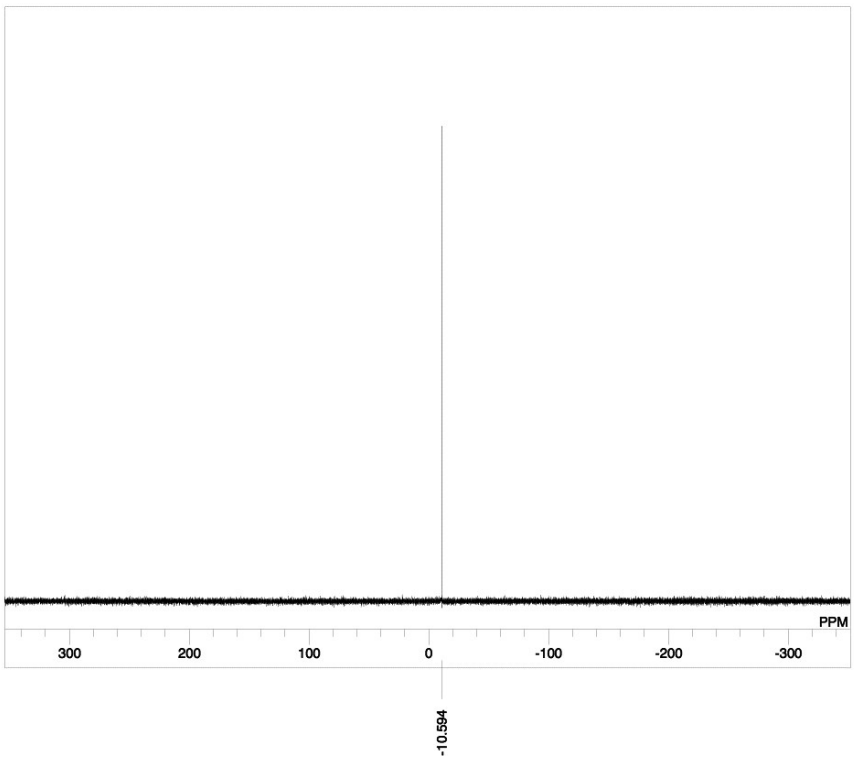

Figure S7. ^{31}P NMR spectrum of **2** in $CDCl_3$.

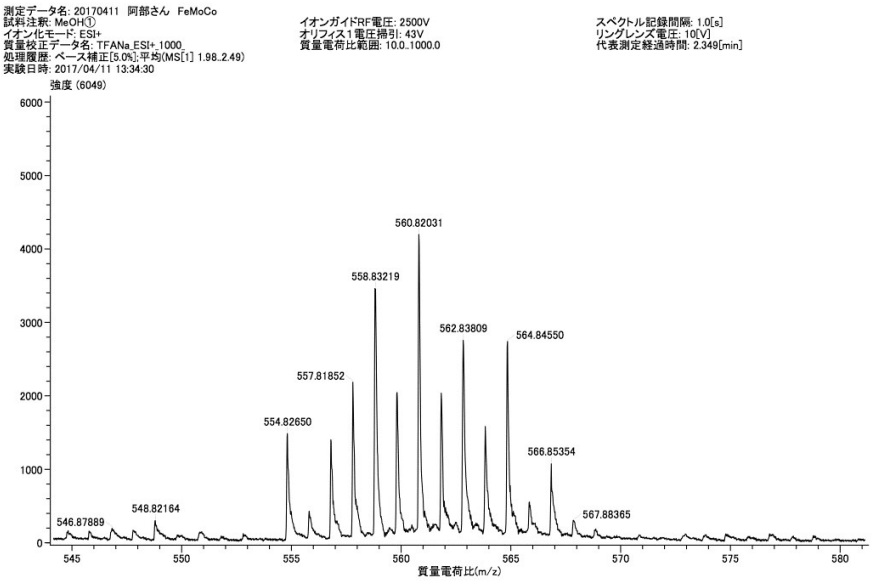

Figure S8. High resolution mass spectrum (ESI-TOF, positive) of **2**.

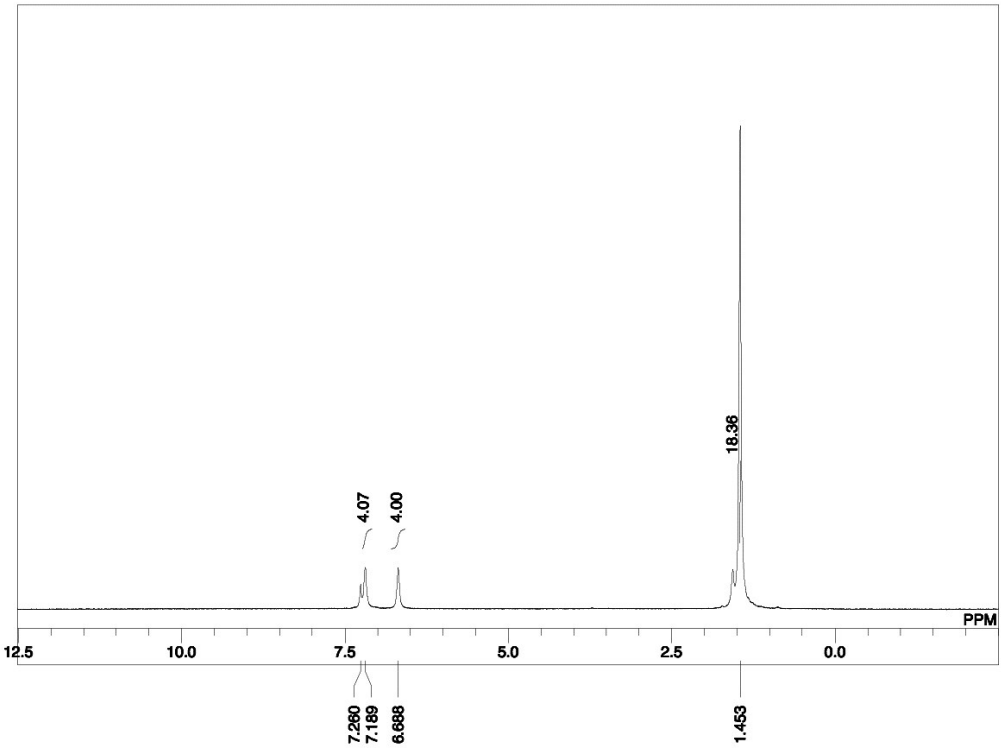

Figure S9. ^{1}H NMR spectrum of **4** in $CDCl_3$.

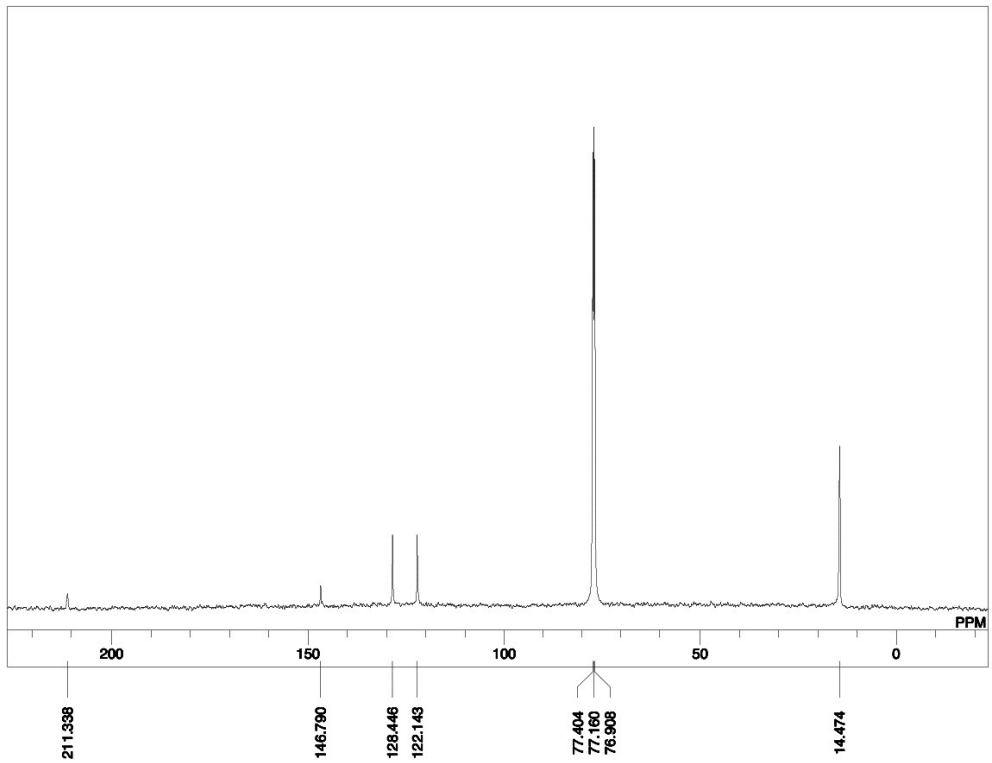

Figure S10. ^{13}C NMR spectrum of **4** in $CDCl_3$.

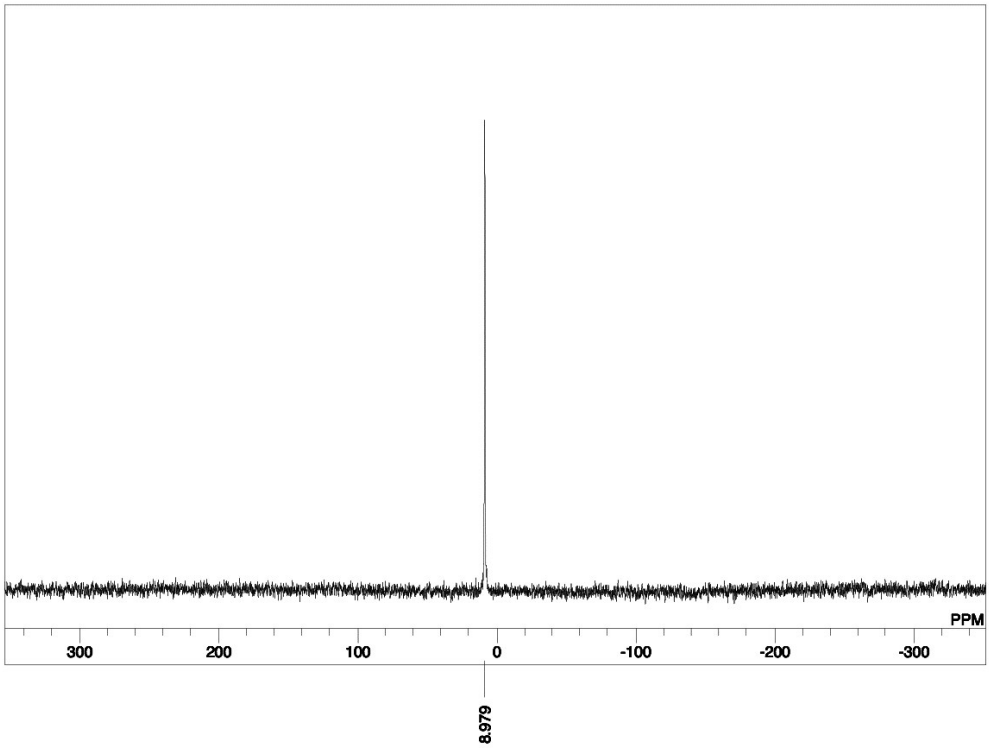

Figure S11. ^{31}P NMR spectrum of **4** in $CDCl_3$.

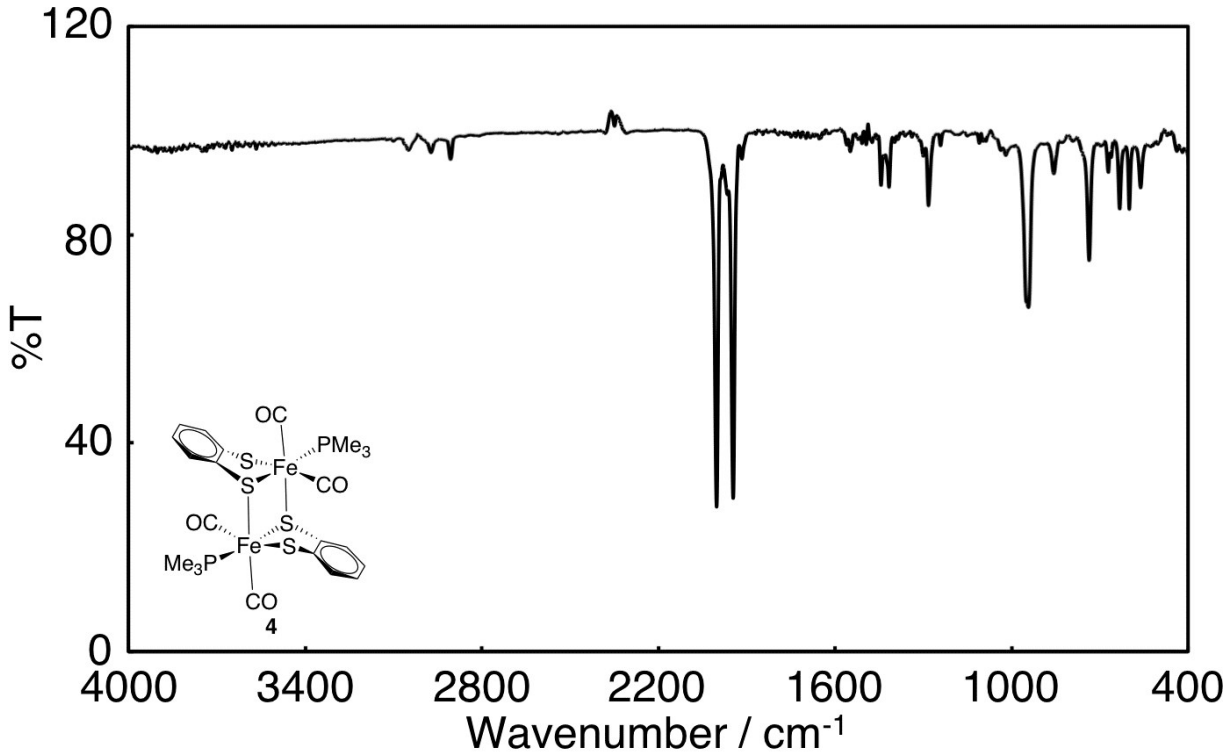

Figure S12. IR spectrum of **4** in a KBr pellet.

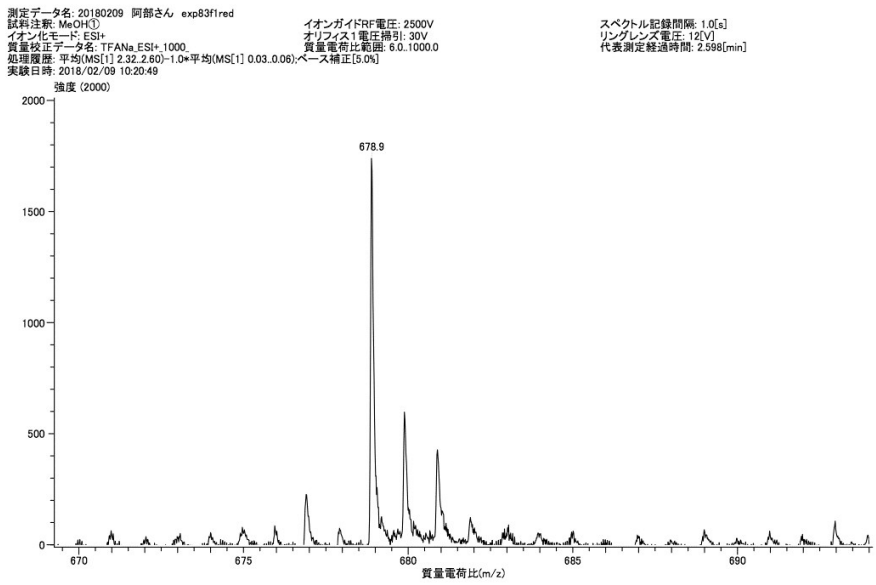

Figure S13. High resolution mass spectrum (ESI-TOF, positive) of **4**.

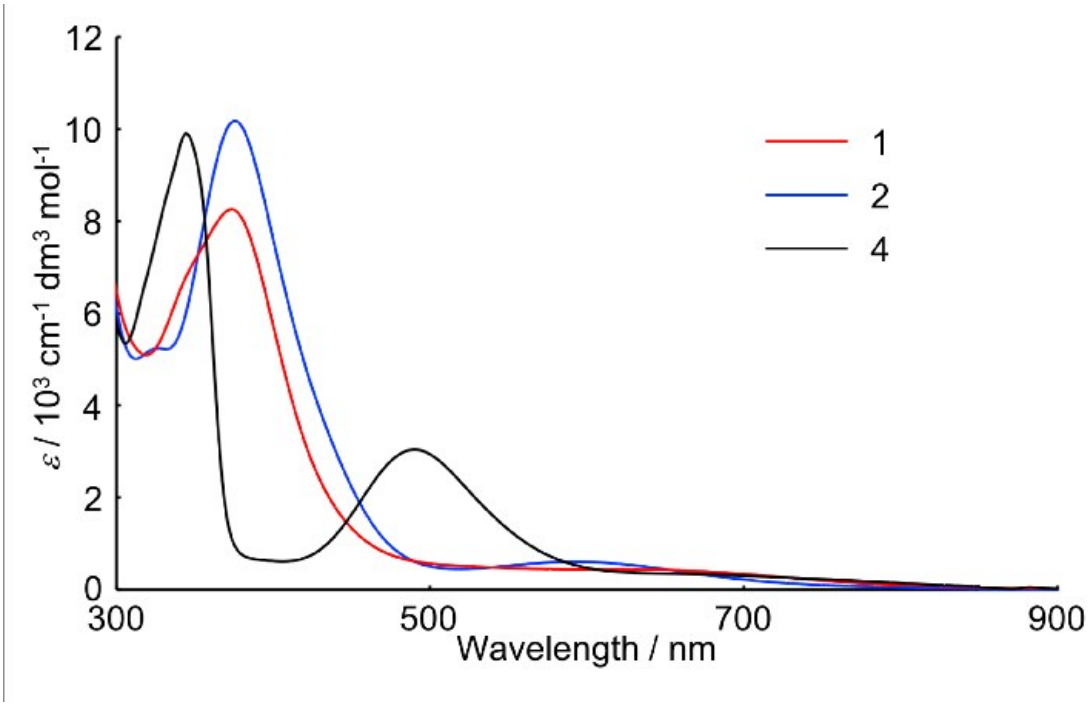

Figure S14. UV-Vis-NIR spectra of **1**, **2** and **4** in toluene.

Table S1. Summary of Crystal data of **1**, **2** and **4**.

□	**1**	**2**	**4**
Empirical formula	$C_{17}H_{22}FeMoO_5P_2S_2$	$C_{15}H_{13}FeMoO_6PS_2$	$C_{22}H_{26}Fe_2O_4P_2S_4$
Formula weight	584.20	536.13	656.31
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Pbca	P2(1)/c	P2(1)/n
a / Å	13.9751(11)	6.4434(6)	9.5169(14)
b / Å	12.7350(10)	17.1407(15)	13.9270(19)
c / Å	25.293(2)	17.5328(16)	10.8610(16)
α / deg	90.00	90.00	90.00
β / deg	90.00	91.3310(10)	110.696(3)
γ / deg	90.00	90.00	90.00
V / Å^3	4501.4(6)	1935.9(3)	1346.6(3)
Z	8	4	2
T / K	103	103	103
D_{calcd} / g cm^{-3}	1.724	1.840	1.619
μ (Mo K_a) / mm^{-1}	1.554	1.723	1.534
F (000)	2352	1064	672
Reflection collected	21635	10471	6740
Independent reflections	4119 (R_{int} = 0.0356)	3918 (R_{int} = 0.0319)	2473 (R_{int} = 0.0896)
*R*1 ($I > 2\sigma(I)$)	0.0325	0.0325	0.0737
w*R*2 (all data)	0.0742	0.0941	0.1616
Goodness of fit on F^2	1.070	1.057	1.075

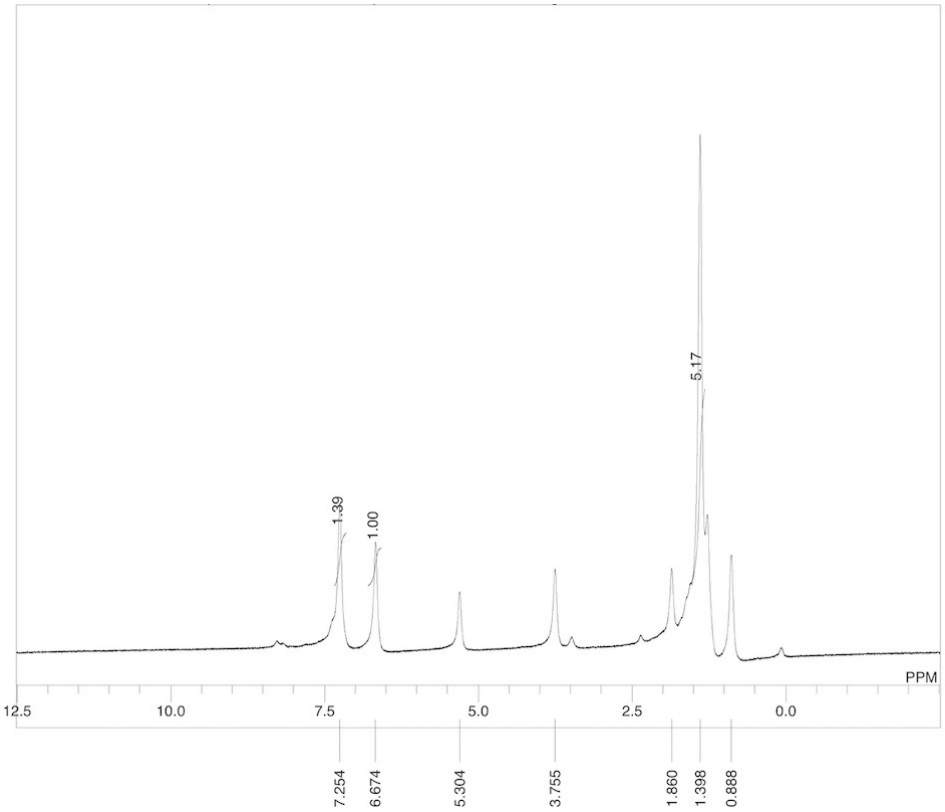

Figure S15. ^{1}H NMR spectrum of the mixture in the reaction of **1** with acetonitrile in $CDCl_3$.

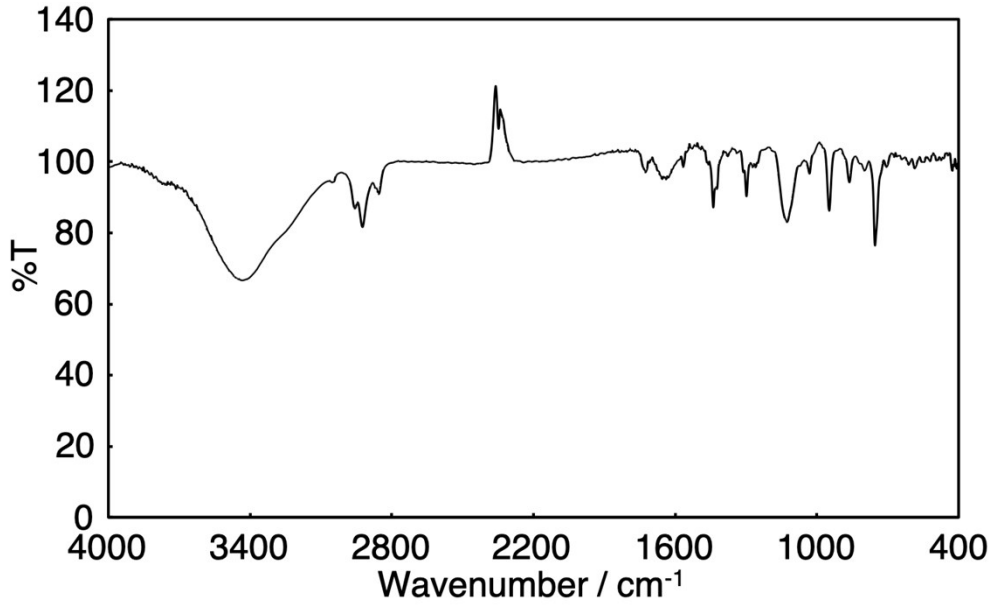

Figure S16. IR spectrum of the mixture in the reaction of **1** with acetonitrile as KBr pellets.

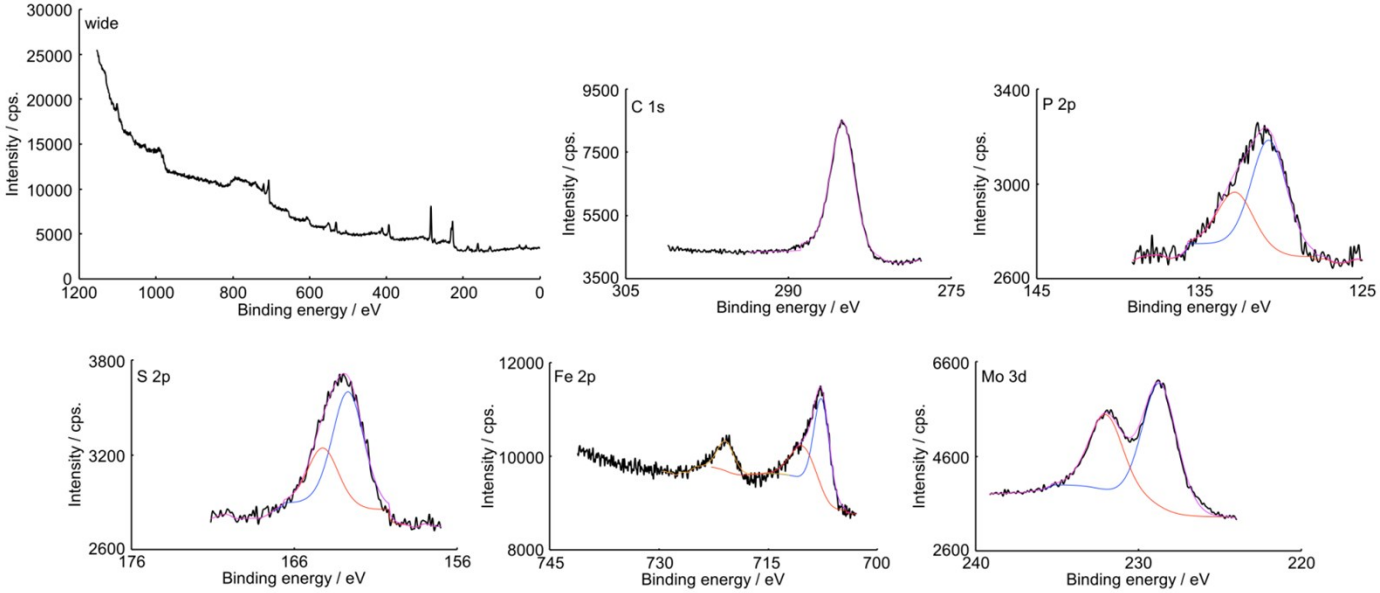

Figure S17. X-ray photoelectron spectra of **1**.

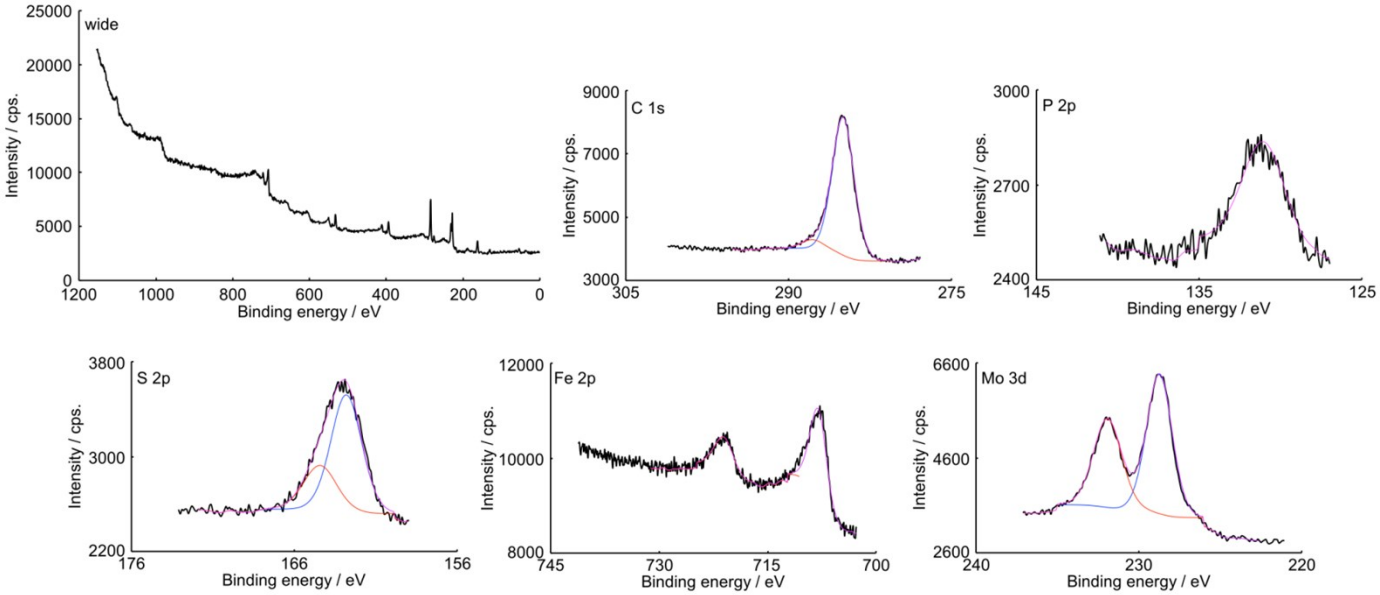

Figure S18. X-ray photoelectron spectra of **2**.

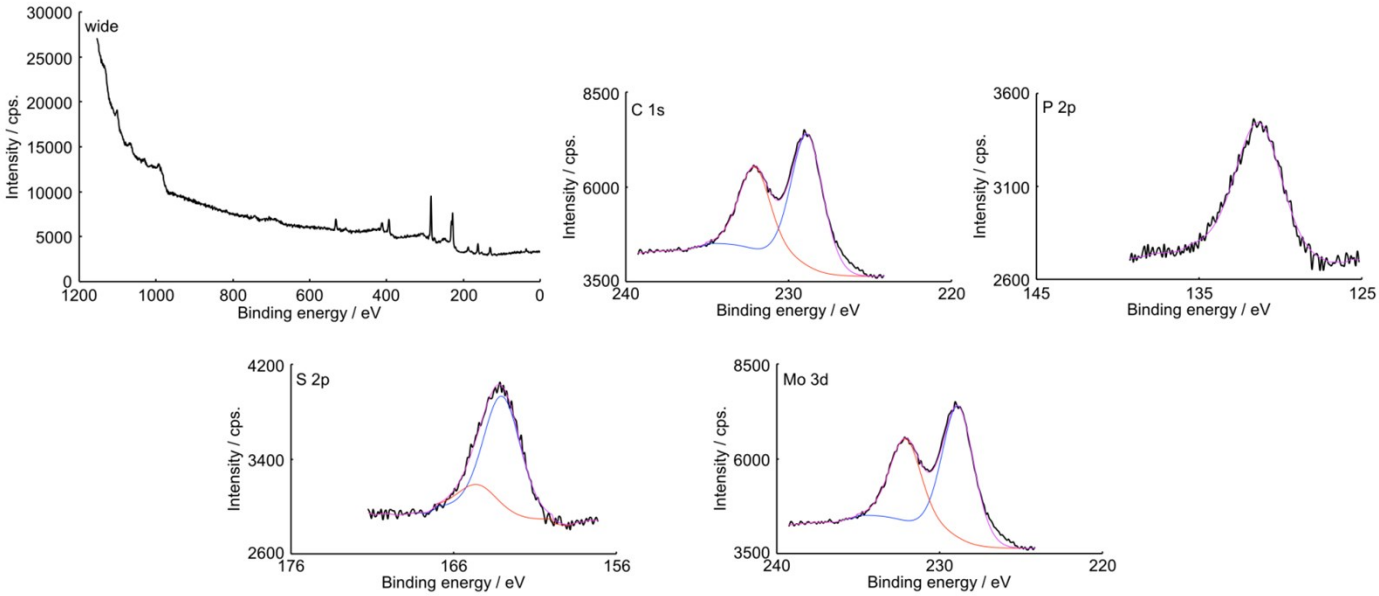

Figure S19. X-ray photoelectron spectra of **3**.