

Electric supplementary information for

Hexanuclear tin(II) and mixed valence tin(II,IV) oxide clusters within polyoxometalates

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General: Cold-spray ionization mass spectra were recorded on JEOL JMS-T100CS. UV-Vis absorption spectra were measured on Jasco V-570 with a quartz cell of 1 cm path length. UV-Vis diffuse reflectance spectra were measured on Jasco V-570DS. Thermogravimetric and differential thermal analyses (TG-DTA) were performed on Rigaku Thermo plus TG 8120. IR spectra were measured on Jasco FT/IR-4100 spectrometer using KBr disks. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses were performed on Shimadzu ICPS-8100. Elemental analyses for C, H, and N were performed on Yanaco MT-6 and Elementar vario MICRO cube at the Elemental Analysis Center of School of Science, the University of Tokyo. GC mass spectra were recorded on Shimadzu GCMS-QP2010 at an ionization voltage of 70 eV.

Reagents: Sn(OAc)₂ and Sn(OAc)₄ (OAc = acetate) were obtained from Wako and used as received. TBAOH (37wt% methanol solution) and nitromethane were obtained from TCI and used as received. Acetonitrile, acetonitrile-*d*₃ (CD₃CN), 1,2-dichloroethane, and diethyl ether were obtained from Kanto. TBA₄H₆[A- α -SiW₉O₃₄] \cdot 2H₂O (**SiW9**, TBA = tetra-*n*-butylammonium) was synthesized according to the reported procedure.^{S1}

Synthesis of TBA₇H[Sn²⁺₆(A- α -SiW₉O₃₄)₂] \cdot 2H₂O (I): Sn(OAc)₂ (0.22 g, 0.93 mmol) was immersed in 1,2-dichloroethane (20 mL), followed by addition of **SiW9** (1.0 g, 0.31 mmol). After

the solution was stirred for 1 day, the solution was poured into diethyl ether (200 mL). The dark orange precipitate formed was filtered off, and dried to afford crude sample of **I**. The crude sample of **I** was recrystallized from a mixed solvent of 1,2-dichloroethane/diethyl ether to afford dark orange crystals of **I** (0.16 g, 15% yield based on **SiW9**). FT-IR (KBr pellet): 2961, 2928, 2874, 2838, 1635, 1483, 1463, 1378, 996, 952, 899, 793, 737, 546, 458, 378, 360, 302, 287, 281, 273, 256, 251 cm^{-1} ; UV-Vis (CH_3CN): λ (ϵ) 251 nm ($7.90 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 418 nm ($1.65 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$); ^{29}Si NMR (CD_3CN , TMS): $\delta = -85.5$ ppm; ^{29}Si NMR (CD_3CN , with 1 eq. of TBAOH 37 wt% in methanol, TMS): $\delta = -86.3$ ppm; ^{119}Sn NMR (CD_3CN , SnCl_4): $\delta = -335.8, -348.5, -350.9, -536.7, -543.3, -548.7$ ppm; ^{119}Sn NMR (CD_3CN , with 1 eq. of TBAOH 37 wt% in methanol, SnCl_4): $\delta = -318.4, -528.6$ ppm with respective integrated intensity ratio of 1:1; ^{183}W NMR (CD_3CN , with 1 eq. of TBAOH 37 wt% in methanol, Na_2WO_4): $\delta = -49.1, -78.8, -83.3, -118.2, -120.7, -134.7$ ppm with respective integrated intensity ratio of 1:1:1:1:1:1; positive ion MS (ESI, acetonitrile): m/z 7106 (calcd. 7106) $[\text{TBA}_8\text{HSn}_6(\text{SiW}_9\text{O}_{34})_2]^+$, 3674 (calcd. 3674) $[\text{TBA}_9\text{HSn}_6(\text{SiW}_9\text{O}_{34})_2]^{2+}$; elemental analysis calcd. (%) for $\text{TBA}_7\text{H}[\text{Sn}_6(\text{SiW}_9\text{O}_{34})_2] \cdot 2\text{H}_2\text{O}$ ($\text{C}_{112}\text{H}_{257}\text{N}_7\text{O}_{70}\text{Si}_2\text{Sn}_6\text{W}_{18}$): C 19.50, H 3.75, N 1.42, Si 0.81, Sn 10.32, W 47.96; found, C 19.49, H 3.70, N 1.45, Si 0.82, Sn 10.42, W 49.25.

Synthesis of $\text{TBA}_7\text{H}[\text{Sn}^{2+}_3\text{Sn}^{4+}_3(\mu_3\text{-O})_3(\text{A-}\alpha\text{-SiW}_9\text{O}_{34})_2] \cdot 3\text{H}_2\text{O}$ (II**):** Compound **I** was dissolved in nitromethane/1,2-dichloroethane (12 mL/3 mL). Then, diethyl ether was added to the solution, followed by filtration with PTFE filter. After the solution was kept at 303 K for 2 days, the yellow crystals formed were filtered off to afford **II** (0.69 g, 65% yield based on **I**). Single crystals suitable for X-ray analysis were obtained by recrystallization from nitromethane/toluene. FT-IR (KBr pellet): 2961, 2925, 2875, 2838, 1635, 1484, 1461, 1402, 1377, 1165, 1109, 1059, 1016, 998, 954, 902, 822, 771, 734, 687, 533, 378, 360, 343, 328, 320, 303, 290, 282, 272, 256 cm^{-1} ; UV-vis (CH_3CN): λ (ϵ) 246 nm ($6.39 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 317 nm ($1.77 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$); ^{29}Si NMR (CD_3CN , with 1 eq. of TBAOH 37 wt% in methanol, TMS): $\delta = -83.3$ ppm ($\Delta_{1/2} = 17.5$ Hz); ^{119}Sn NMR

(CD₃CN, SnCl₄): $\delta = -498.7, -544.4, -605.2, -631.6$ ppm with respective integrated intensity ratio of 1:2:1:2; ¹¹⁹Sn NMR (CD₃CN, with 1 eq. of TBAOH 37 wt% in methanol, SnCl₄): $\delta = -500.0, -633.8$ ppm with respective integrated intensity ratio of 1:1; ¹⁸³W NMR (CD₃CN, with 1 eq. of TBAOH 37 wt% in methanol, Na₂WO₄): $\delta = -119.6, -145.0$ ppm with respective integrated intensity ratio of 2:1; positive ion MS (CSI, acetonitrile): m/z 7154 (calcd. 7154) [TBA₈HSn₆O₃(SiW₉O₃₄)₂]⁺, 3698 (calcd. 3698) [TBA₉HSn₆O₃(SiW₉O₃₄)₂]²⁺; elemental analysis calcd. (%) for TBA₇H[Sn₆O₃(SiW₉O₃₄)₂] \cdot 3H₂O (C₁₁₂H₂₅₉N₇O₇₄Si₂Sn₆W₁₈): C 19.31, H 3.75, N 1.41, Si 0.81, Sn 10.23, W 47.50; found, C 19.45, H 3.70, N 1.51, Si 0.81, Sn 10.33, W 48.13.

X-ray crystallography: Diffraction measurements were made on a Rigaku MicroMax-007 Saturn 724 CCD detector with graphite monochromated Mo K α radiation ($\lambda = 0.71069$ Å) at -153 K. Data were collected and processed using CrystalClear^{S2} and HKL2000.^{S3} Neutral scattering factors were obtained from the standard source. In the reduction of data, Lorentz and polarization corrections were made. The structural analysis was performed using CrystalStructure^{S4} and Win-GX.^{S5} All structures were solved by SHELXS and refined by full-matrix least-squares methods using SHELXL.^{S6} The highly disordered solvent molecules of crystallization were omitted by use of SQUEEZE program.^{S7} CCDC-1486719 (**I**) and CCDC-1486720 (**II**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Bond valence sum (BVS) calculations: The BVS values were calculated by the expression for the variation of the length r_{ij} of a bond between two atoms i and j in observed crystal with valence V_i :

$$V_i = \sum_j \exp\left(\frac{r'_0 - r_{ij}}{B}\right)$$

where B is constant equal to 0.37 Å, r'_0 is bond valence parameter for a given atom pair.^{S8}

DFT calculations: The calculations were performed with Gaussian 09 software.^{S9} The anionic parts of **I**, **II**, and **SiW9** were optimized at the B3LYP level theory^{S10} with 6-31++G* (for O, H) and 6-31G* (for Si), and LanL2DZ (for Sn, W)^{S11} by using the polarizable continuum model (PCM) using the integral equation formalism variant (IEFPCM)^{S12} with the parameters of the United Atom Topological Model (UAHF) for acetonitrile.

Electrochemistry: Cyclic voltammetric measurements were carried out with a Solartron SI 1287 Electrochemical Interface. A standard three-electrode arrangement was employed with a BAS glassy carbon disk electrode as the working electrode, a platinum wire as the counter electrode, and a silver wire electrode as the pseudoreference electrode. The voltage scan rate was set at 200 mV s⁻¹, and TBAClO₄ was used as an electrolyte. The potentials were measured using Ag/AgNO₃ reference electrode (10 mM AgNO₃, 100 mM TBAClO₄ in acetonitrile, 0.55 V vs NHE)

Additional references

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Table S1. Crystallographic data for **I** and **II**

	I	II
formula	C ₁₂₄ Cl ₁₂ N ₇ O ₇₃ Si ₂ Sn ₆ W ₁₈	C ₁₁₅ N ₁₀ O ₇₇ Si ₂ Sn ₆ W ₁₈
Fw (g mol ⁻¹)	7258.33	6830.87
crystal system	monoclinic	triclinic
space group	<i>P</i> 2 ₁ (No. 4)	<i>P</i> -1 (No. 2)
<i>a</i> (Å)	18.75170(10)	17.6999(2)
<i>b</i> (Å)	28.4384(3)	18.7362(2)
<i>c</i> (Å)	21.5390(2)	29.8744(4)
α (deg)	90	82.6590(10)
β (deg)	115.1216(3)	88.2780(10)
γ (deg)	90	74.2910(10)
<i>V</i> (Å ³)	10399.58(16)	9458.9(2)
<i>Z</i>	2	2
temp (K)	113(2)	113(2)
ρ_{calcd} (g cm ⁻³)	2.318	2.398
GOF	1.038	1.048
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0724 (for 24462 data)	0.0767 (for 35730 data)
<i>wR</i> ₂	0.2046 (for all 28615 data)	0.2039 (for all 51684 data)

Table S2. Selected BVS values for **I** and **II**

I		II	
Sn1	2.26	Sn1	1.93
Sn2	1.87	Sn2	1.84
Sn3	2.31	Sn3	2.02
Sn4A	1.86	Sn4	3.91
Sn5A	1.85	Sn5	3.91
Sn6A	1.86	Sn6	3.94
Sn4B	2.01		
Sn5B	2.01		
Sn6B	2.01		

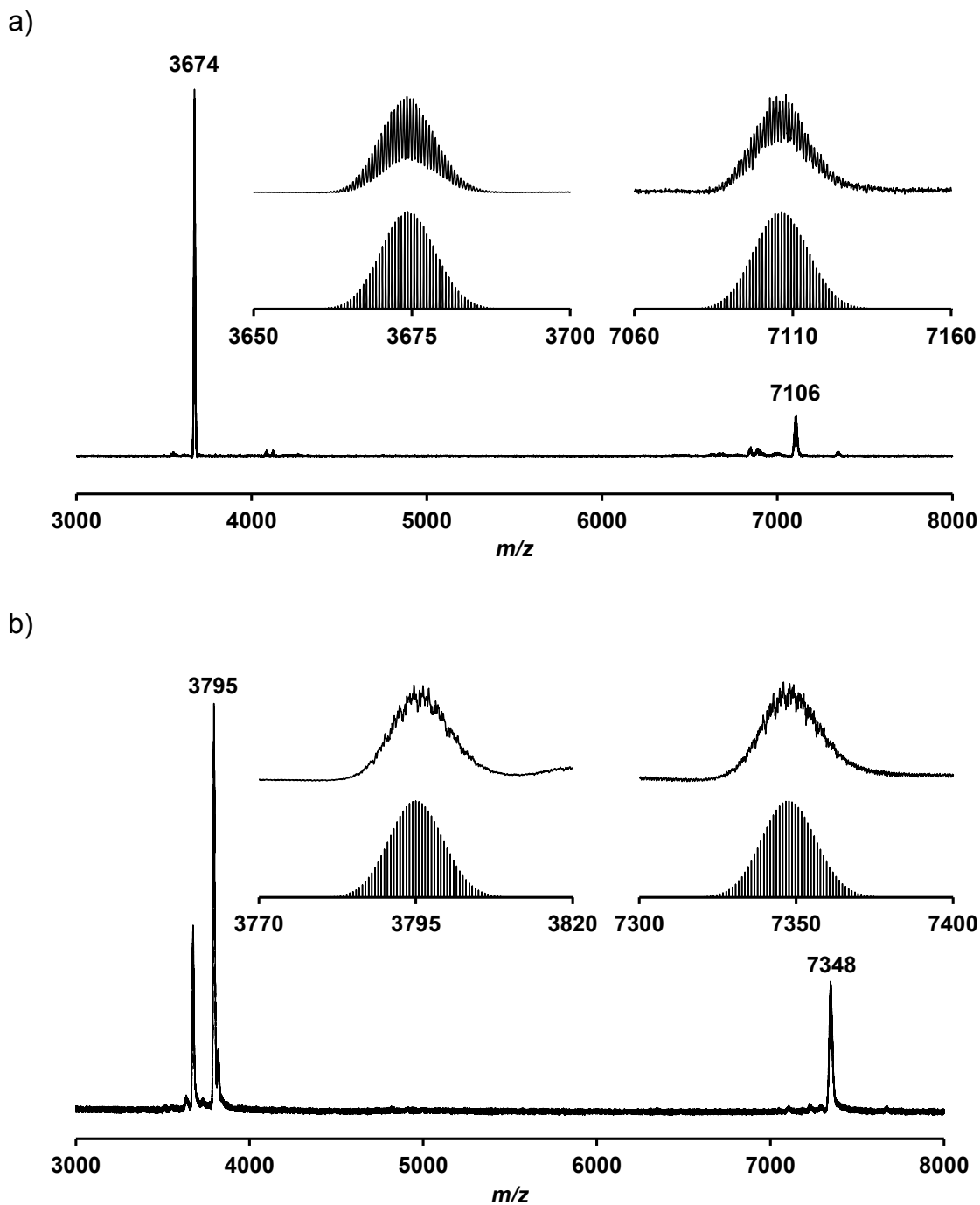


Fig. S1 CSI-mass spectra of a) **I** and b) **I** + TBAOH (1 equiv) in acetonitrile. Insets: a) spectra in the range of m/z 3650–3700 and 7060–7160, and the calculated patterns for $[\text{TBA}_9\text{HSn}_6(\text{SiW}_9\text{O}_{34})_2]^{2+}$ (m/z 3674) and $[\text{TBA}_8\text{HSn}_6(\text{SiW}_9\text{O}_{34})_2]^+$ (m/z 7106), b) spectra in the range of m/z 3675–2725 and 7110–7210, and the calculated patterns for $[\text{TBA}_{10}\text{Sn}_6(\text{SiW}_9\text{O}_{34})_2]^{2+}$ (m/z 3795) and $[\text{TBA}_9\text{Sn}_6(\text{SiW}_9\text{O}_{34})_2]^+$ (m/z 7348).

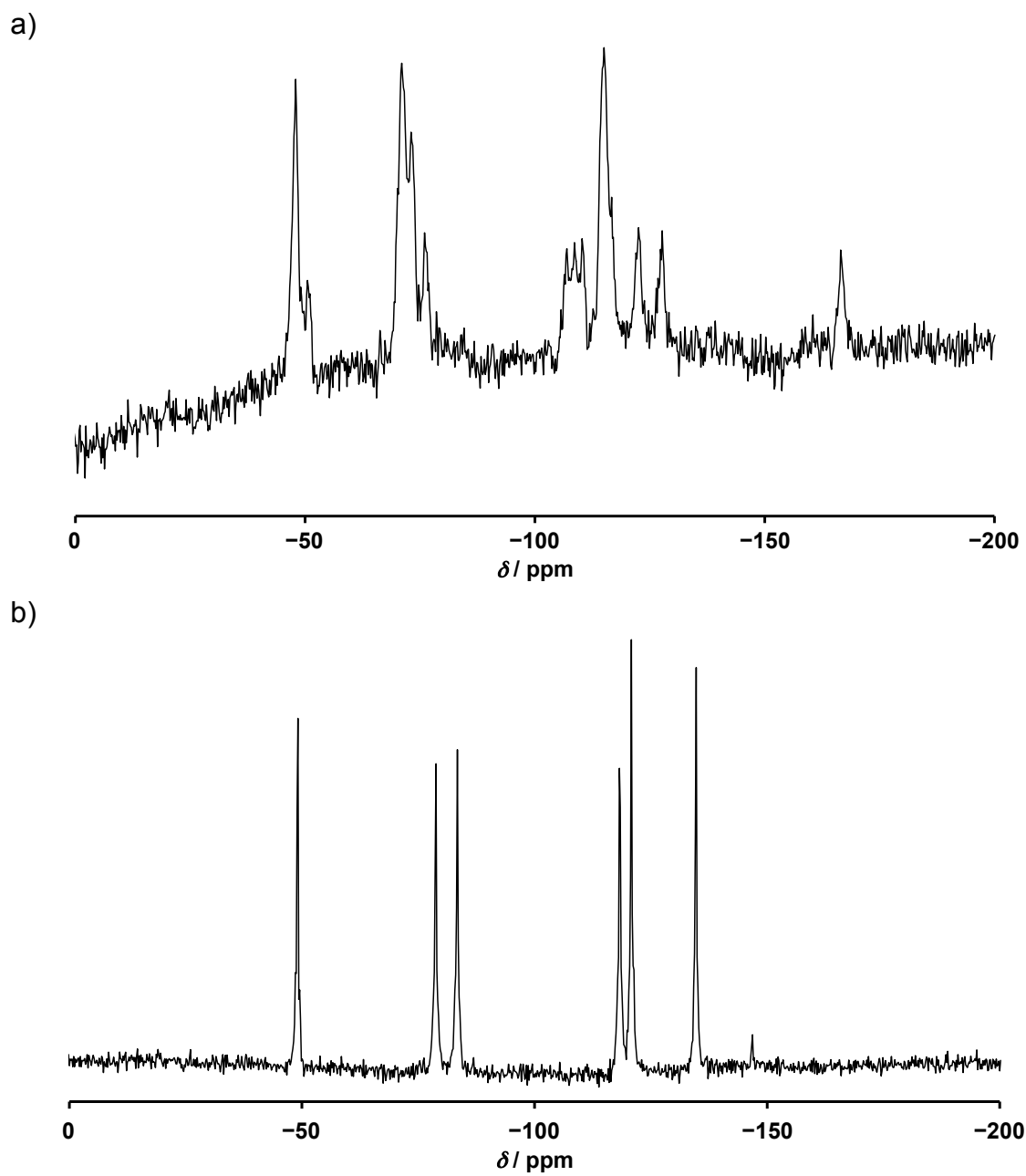
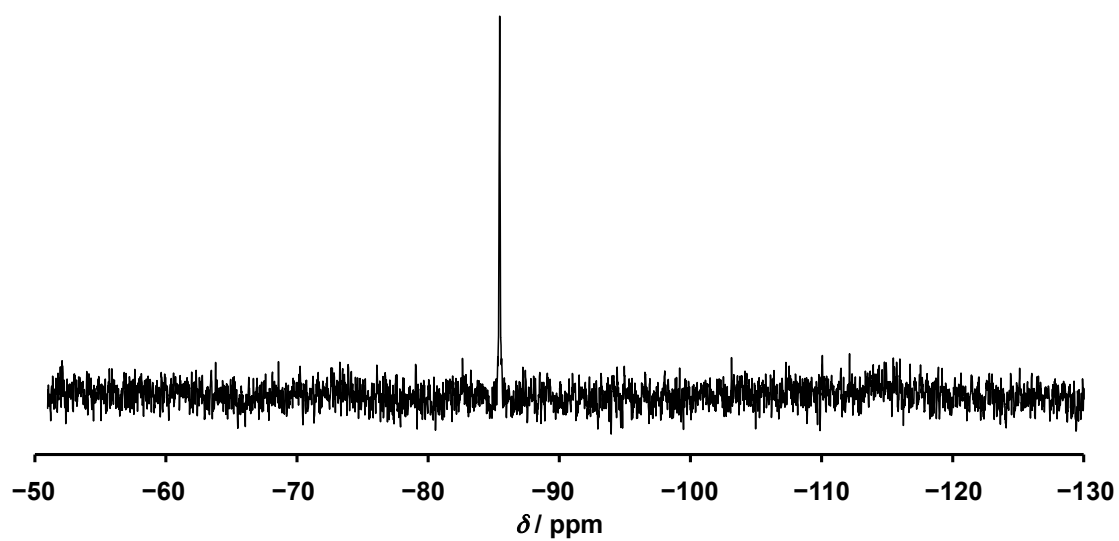


Fig. S2. ^{183}W NMR spectra of a) **I** and b) **I** + TBAOH (1 equiv with respect to **I**) in acetonitrile- d_3 .

a)



b)

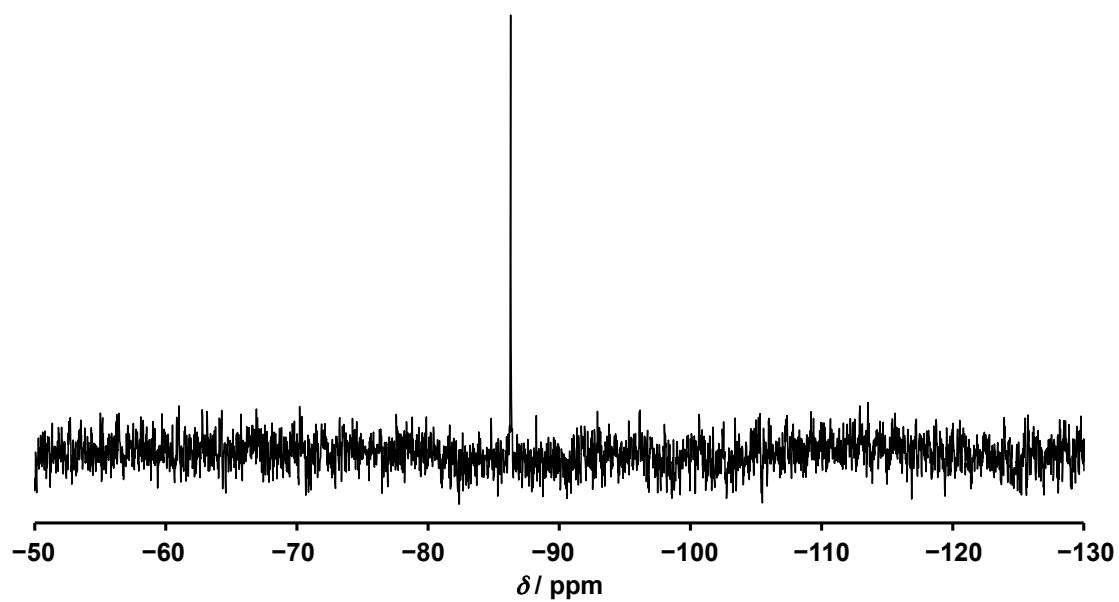


Fig. S3 ^{29}Si NMR spectra of a) **I** and b) **I** + TBAOH (1 equiv with respect to **I**) in acetonitrile- d_3 .

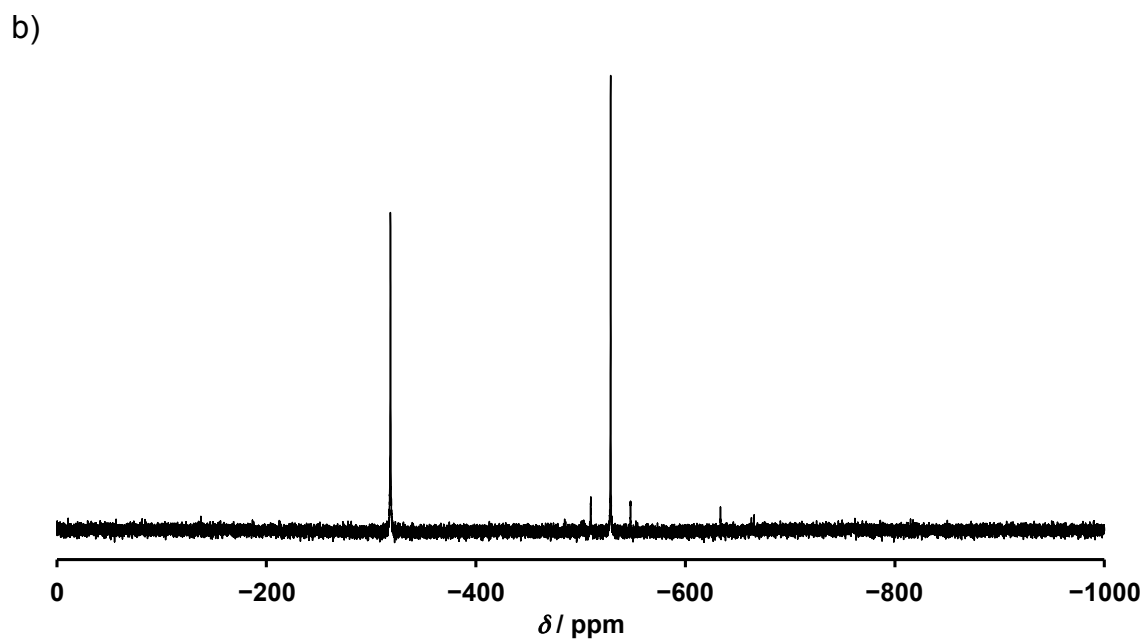
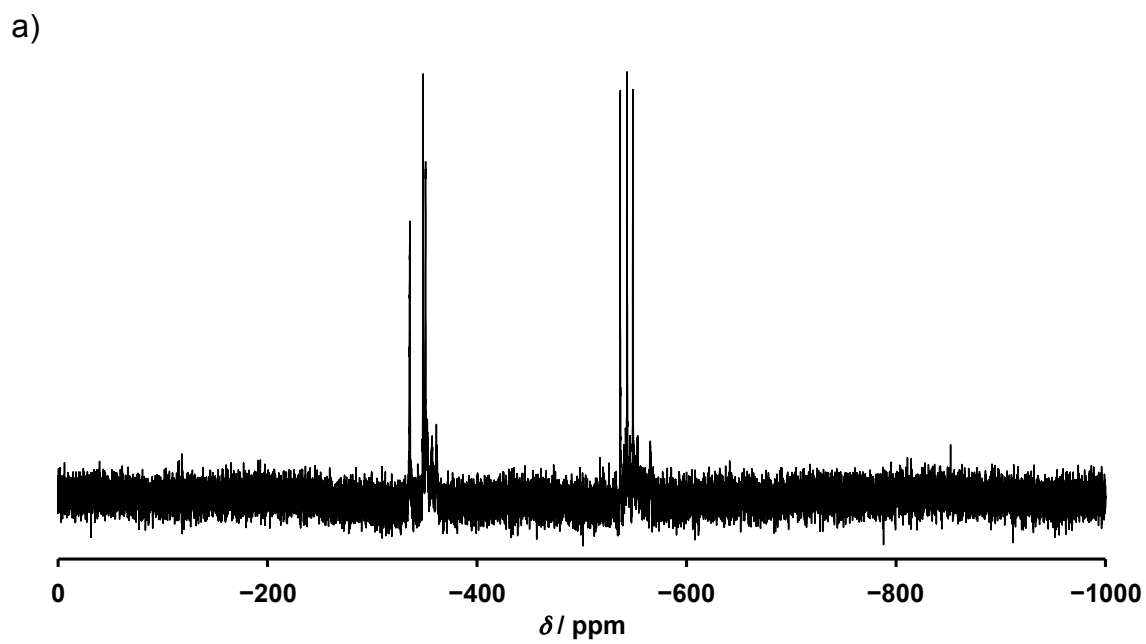


Fig. S4 ^{119}Sn NMR spectra of a) **I** and b) **I** + TBAOH (1 equiv with respect to **I**) in acetonitrile- d_3 .

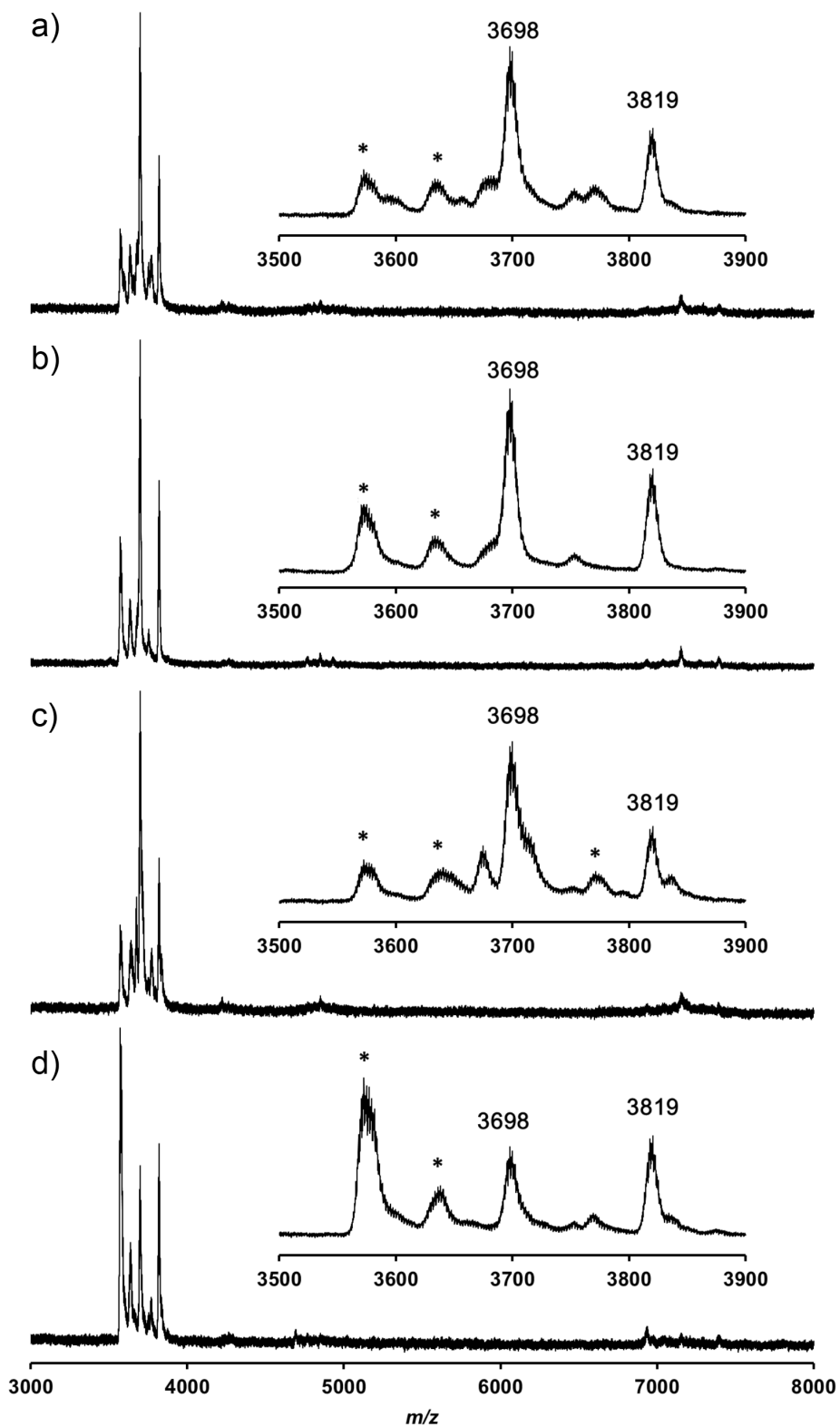


Fig. S5 CSI-mass spectra of **I** after addition of H_2O_2 (a, 5 min; b, 8 h) and *tert*-butyl hydroperoxide (c, 5 min; d, 8 h) (3 equivalents with respect to **I**) in acetonitrile. Signal sets centered at m/z 3698 and 3819 are assignable to $[\text{TBA}_9\text{HSn}_6\text{O}_3(\text{SiW}_9\text{O}_{34})_2]^{2+}$ and $[\text{TBA}_{10}\text{Sn}_6\text{O}_3(\text{SiW}_9\text{O}_{34})_2]^{2+}$, respectively. Signals indicated by asterisks could not be assigned.

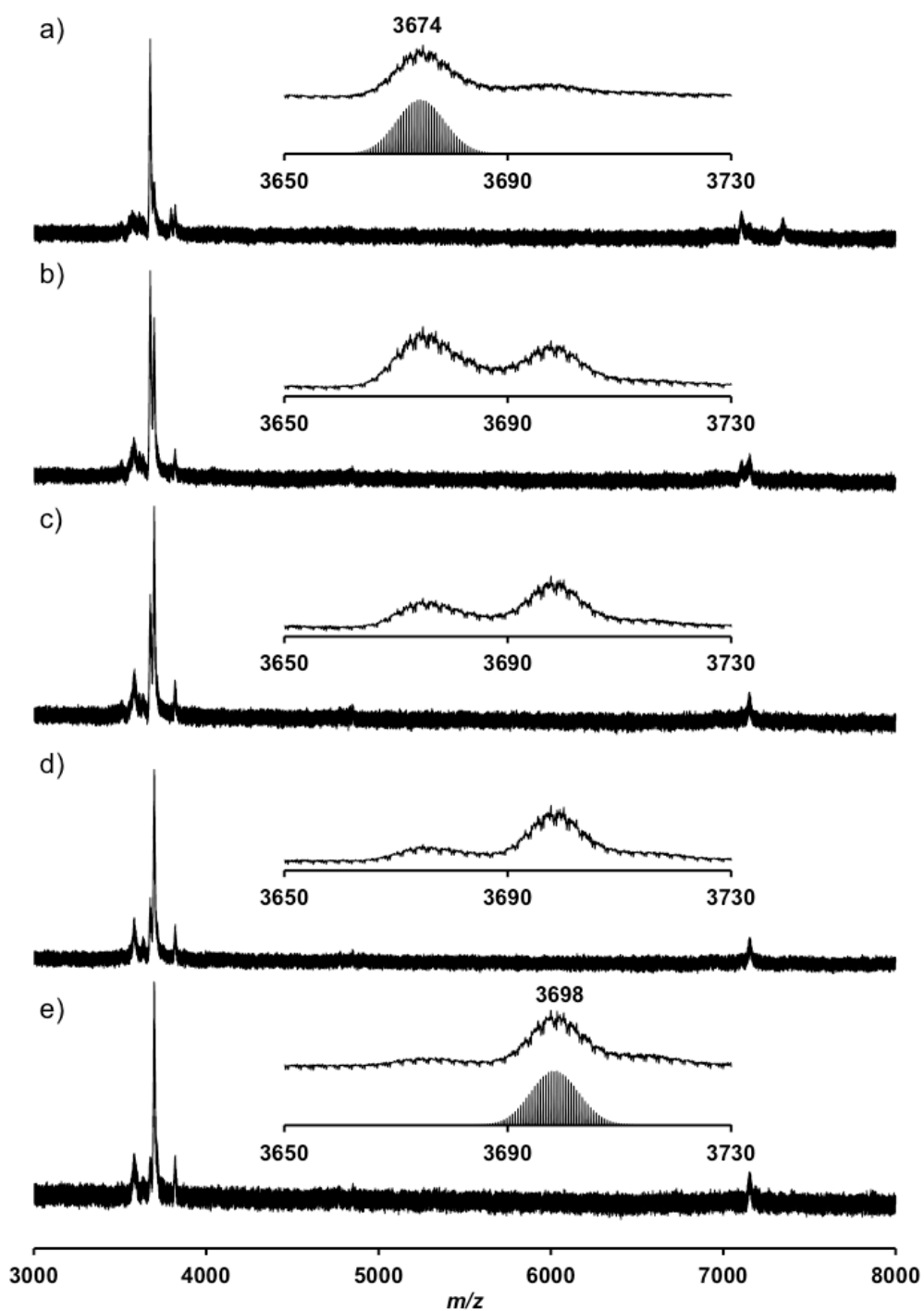


Fig. S6 CSI-mass spectra of **I** treated in the mixed solvent of nitromethane/1,2-dichloroethane (4:1 v/v) for a) 0 h, b) 2 h, c) 4 h, d) 6 h, and e) 8 h. Insets: spectra in the range of m/z 3650–3730 and the calculated patterns for $[\text{TBA}_9\text{HSn}_6(\text{SiW}_9\text{O}_{34})_2]^{2+}$ (m/z 3674) and $[\text{TBA}_9\text{HSn}_6\text{O}_3(\text{SiW}_9\text{O}_{34})_2]^{2+}$ (m/z 3698).

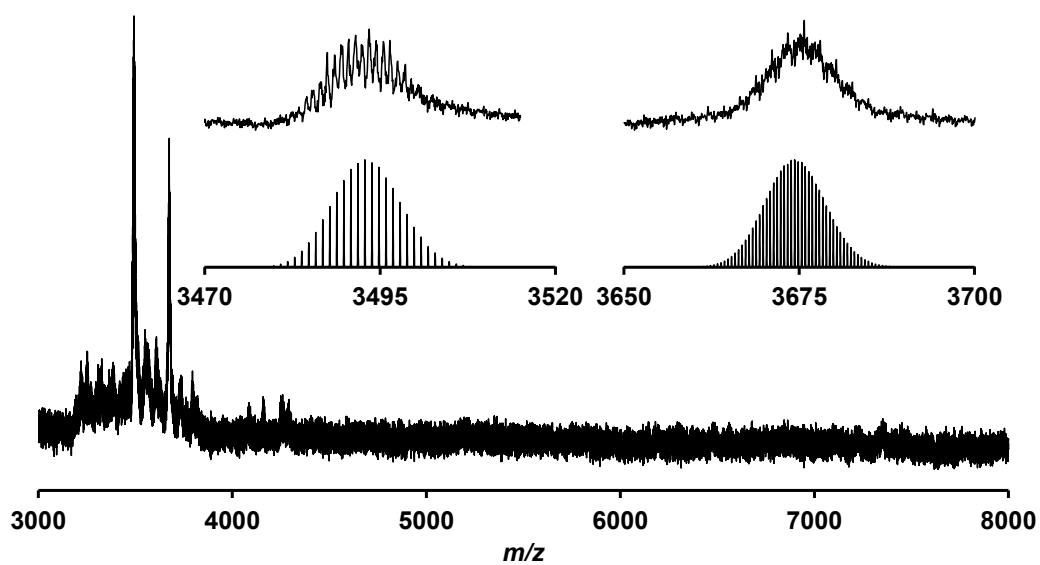


Fig. S7 CSI-mass spectrum of the product by the reaction of **SiW9**, Sn(OAc)₂, and Sn(OAc)₄ (2:3:3 molar ratio) in acetonitrile. Insets: spectra in the range of *m/z* 3470–3520 and 3650–3700, and the calculated patterns for [TBA₅SiW₉O₃₀(CH₃COO)₂]⁺ (*m/z* 3693) and [TBA₉HSn₆(SiW₉O₃₄)₂]²⁺ (*m/z* 3674).

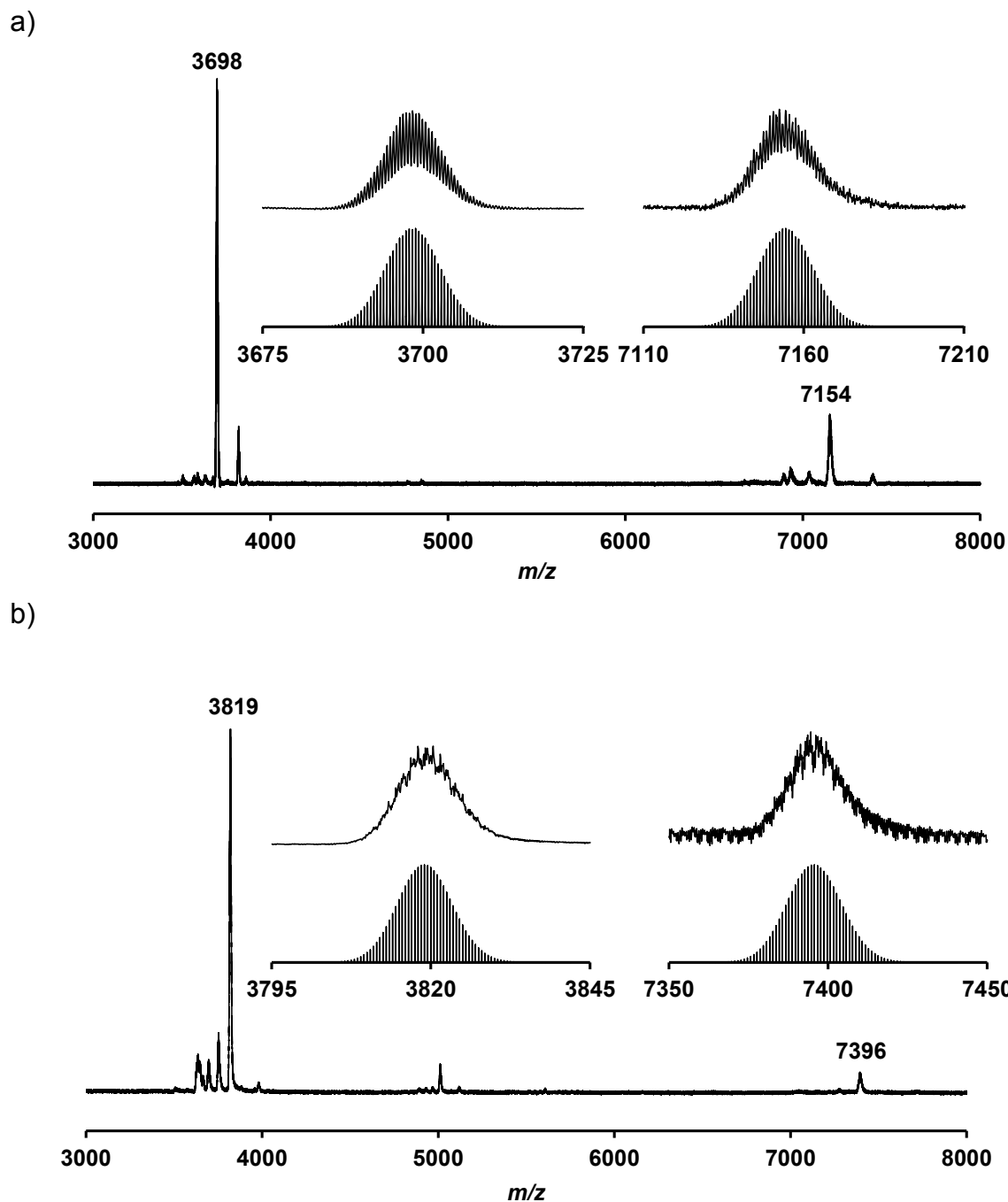
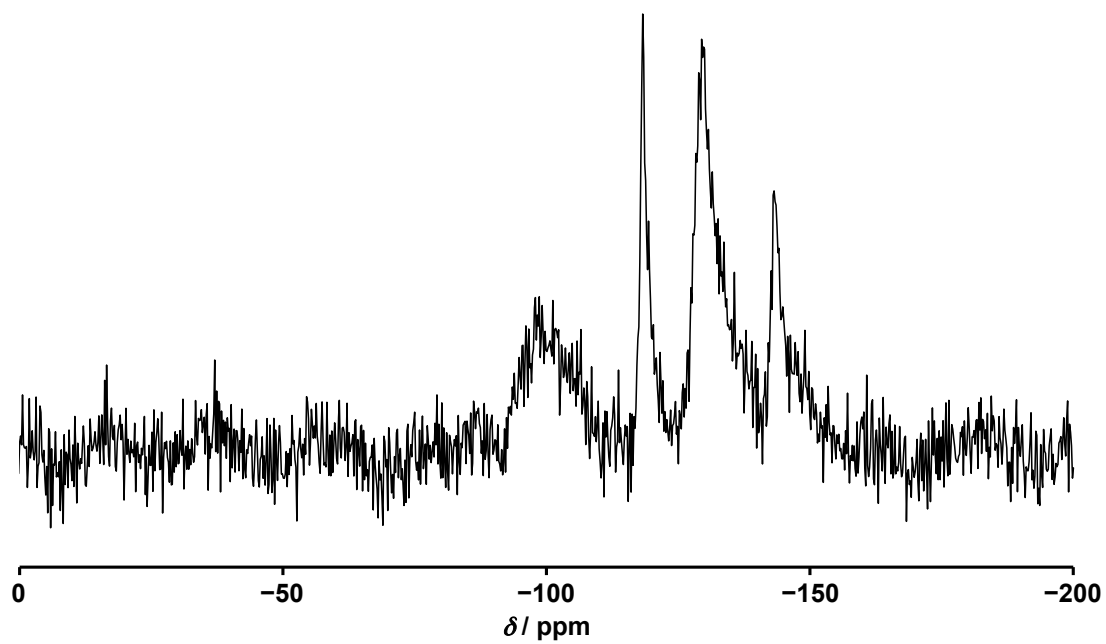


Fig. S8 CSI-mass spectra of a) **II** and b) **II** + TBAOH (1 equiv) in acetonitrile. Insets: a) spectra in the range of *m/z* 3675–3725 and 7110–7210, and the calculated patterns for $[\text{TBA}_9\text{HSn}_6\text{O}_3(\text{SiW}_9\text{O}_{34})_2]^{2+}$ (*m/z* 3698) and $[\text{TBA}_8\text{HSn}_6\text{O}_3(\text{SiW}_9\text{O}_{34})_2]^+$ (*m/z* 7154), b) spectra in the range of *m/z* 3795–3845 and 7350–7450, and the calculated patterns for $[\text{TBA}_{10}\text{Sn}_6\text{O}_3(\text{SiW}_9\text{O}_{34})_2]^{2+}$ (*m/z* 3819) and $[\text{TBA}_9\text{Sn}_6\text{O}_3(\text{SiW}_9\text{O}_{34})_2]^+$ (*m/z* 7396).

a)



b)

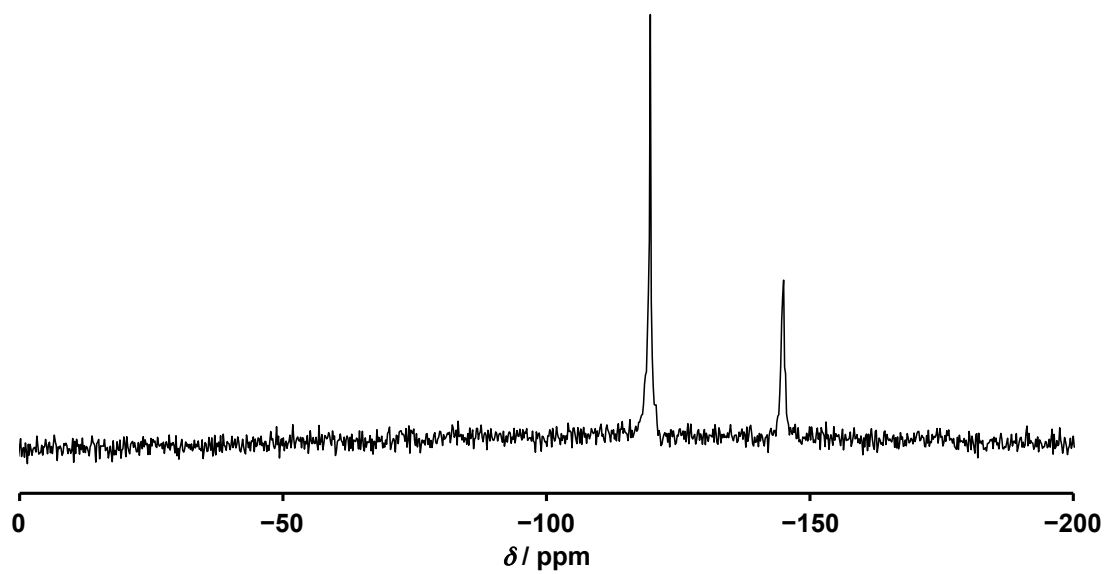
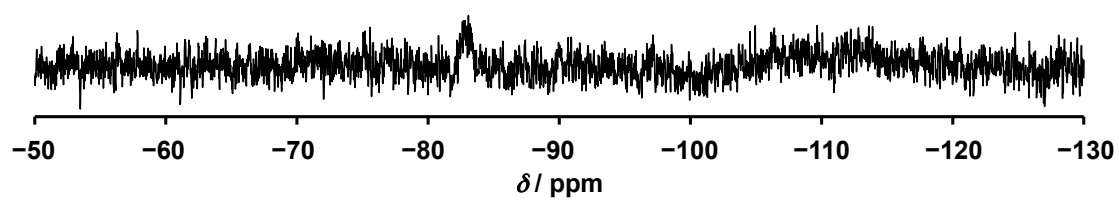


Fig. S9 ^{183}W NMR spectra of a) **II** and b) **II** + TBAOH (1 equiv with respect to **II**) in acetonitrile- d_3 .

a)



b)

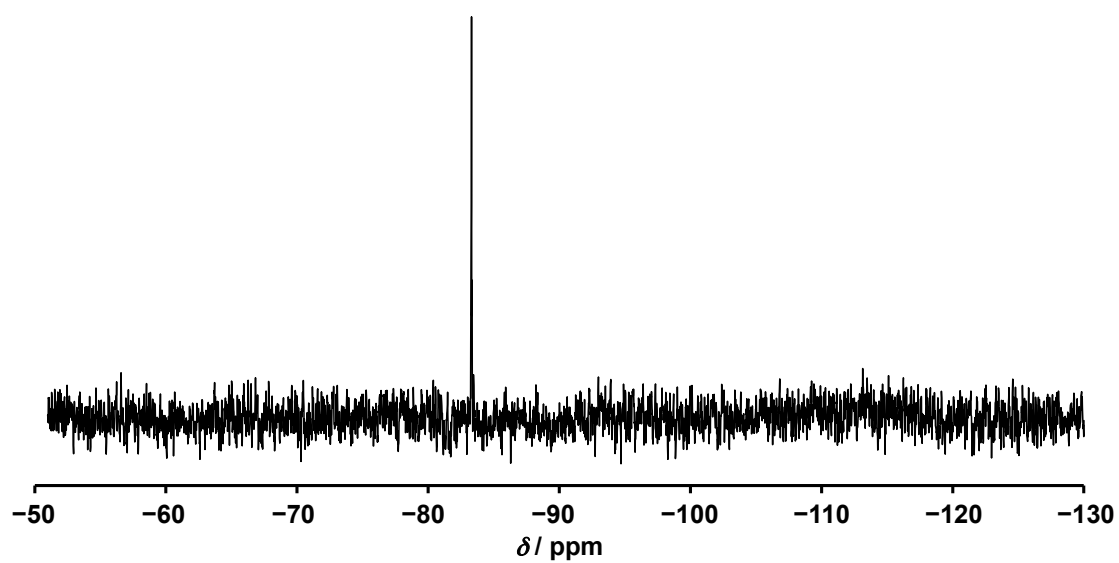
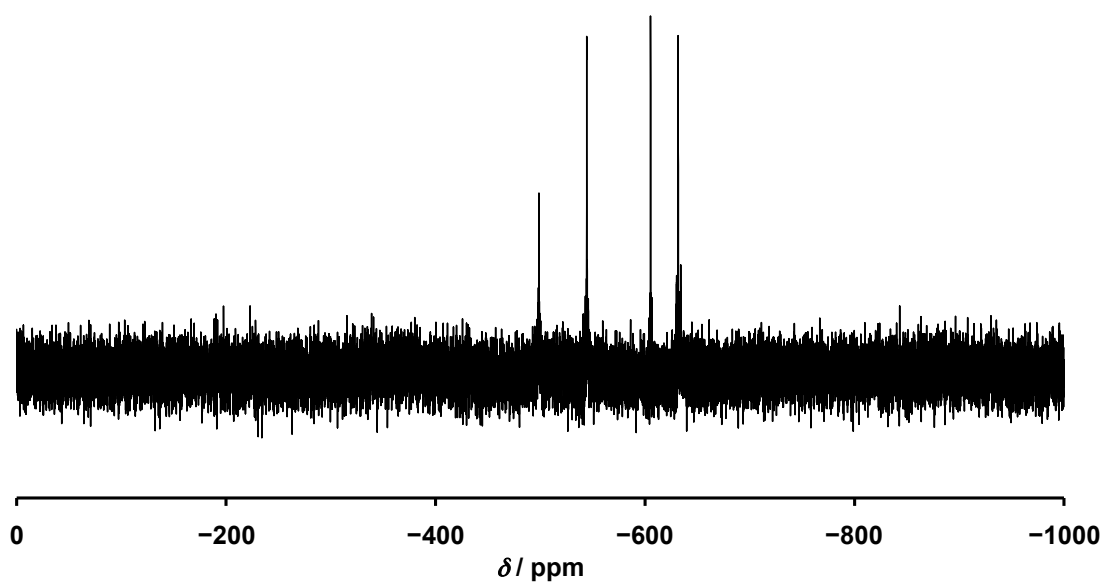


Fig. S10 ^{29}Si NMR spectra of a) **II** and b) **II** + TBAOH (1 equiv with respect to **II**) in acetonitrile- d_3 .

a)



b)

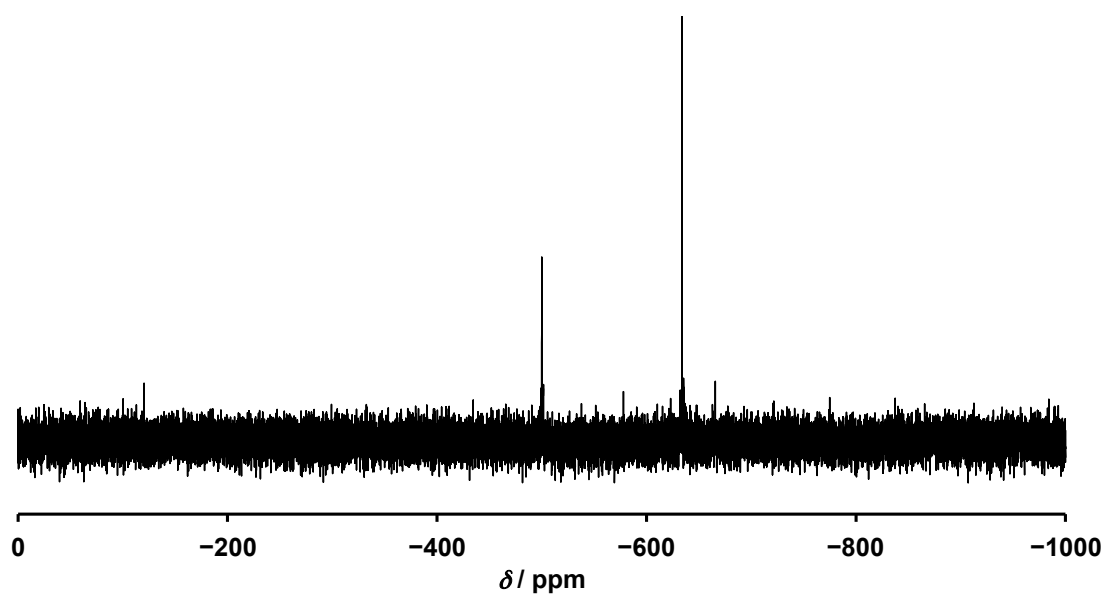


Fig. S11 ^{119}Sn NMR spectra of a) **II** and b) **II** + TBAOH (1 equiv with respect to **II**) in acetonitrile- d_3 .

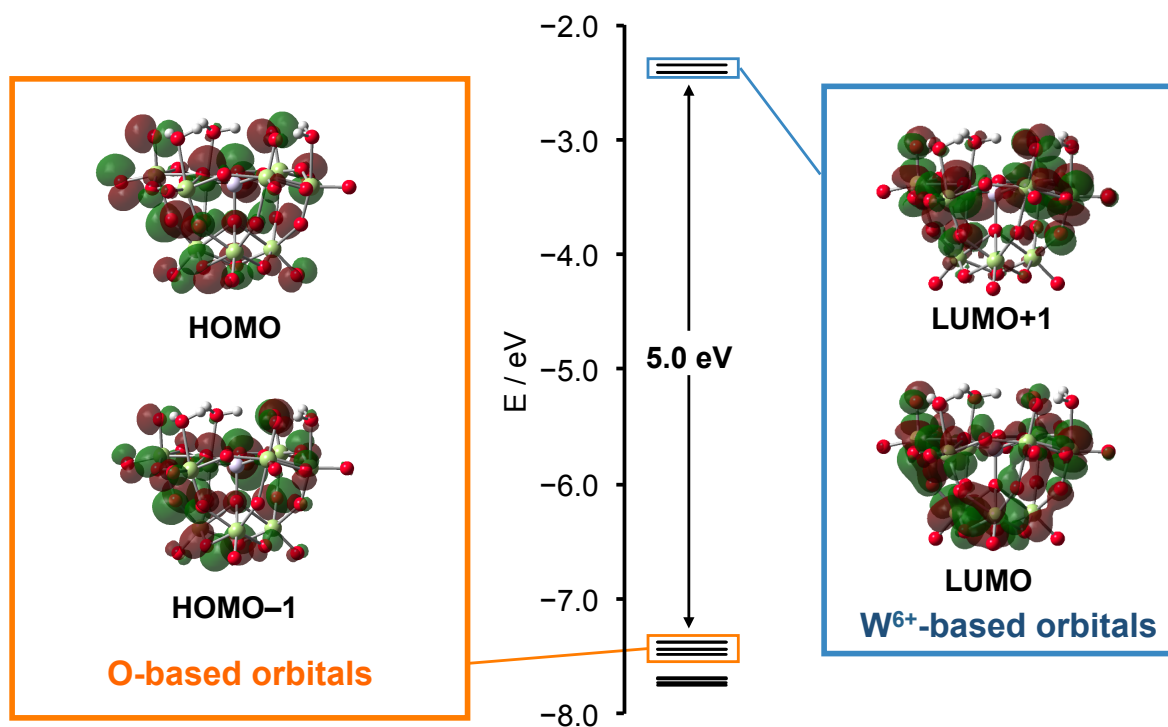
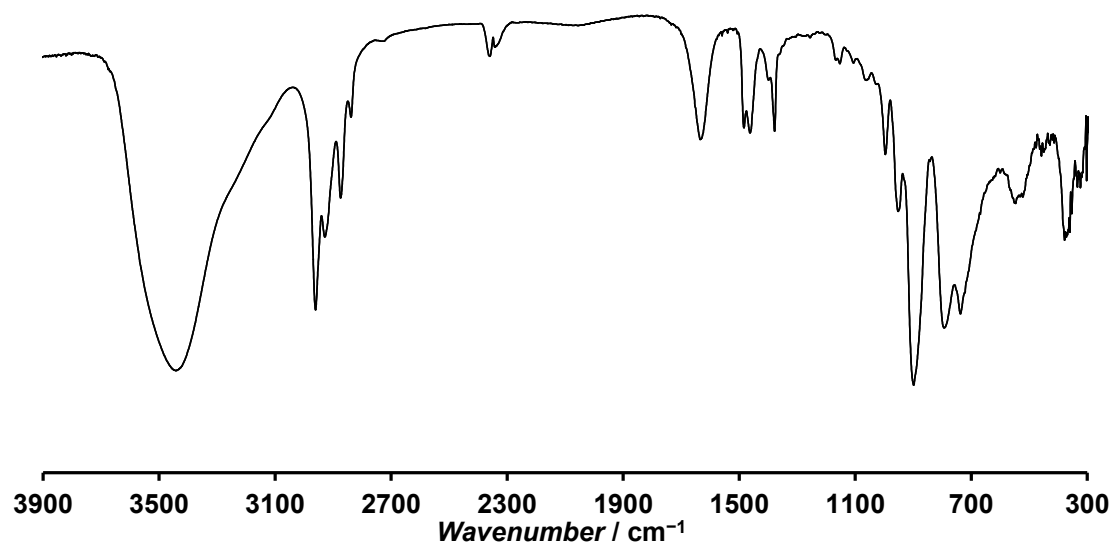


Fig. S12 Energy diagram and molecular orbitals of **SiW9**. Gray, light green, and red spheres represent Si, W, and O atoms, respectively,

a)



b)

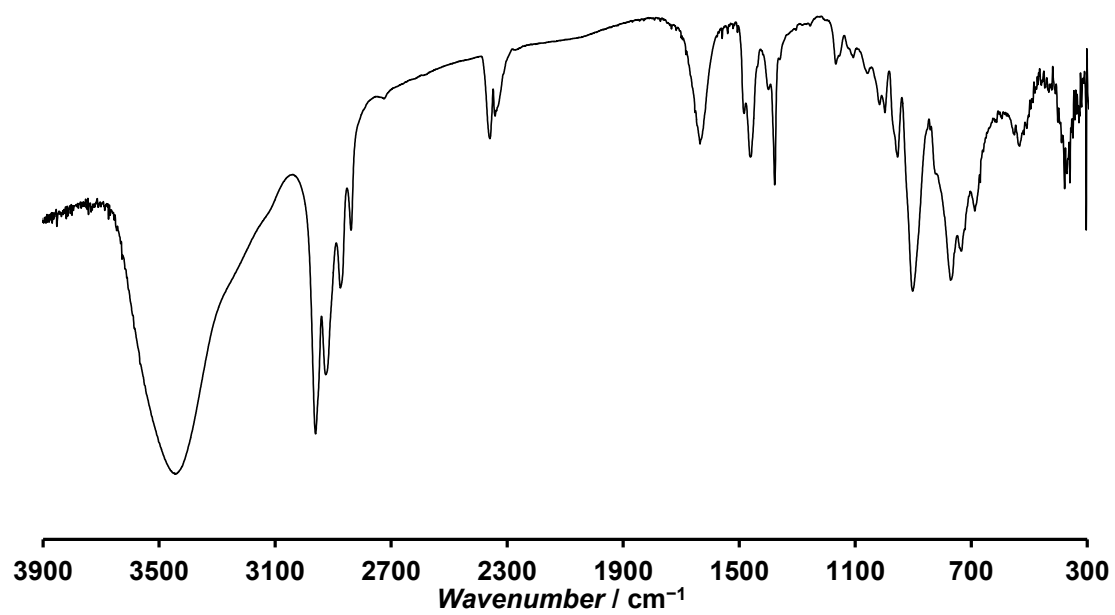


Fig. S13 IR spectra of a) **I** and b) **II**.

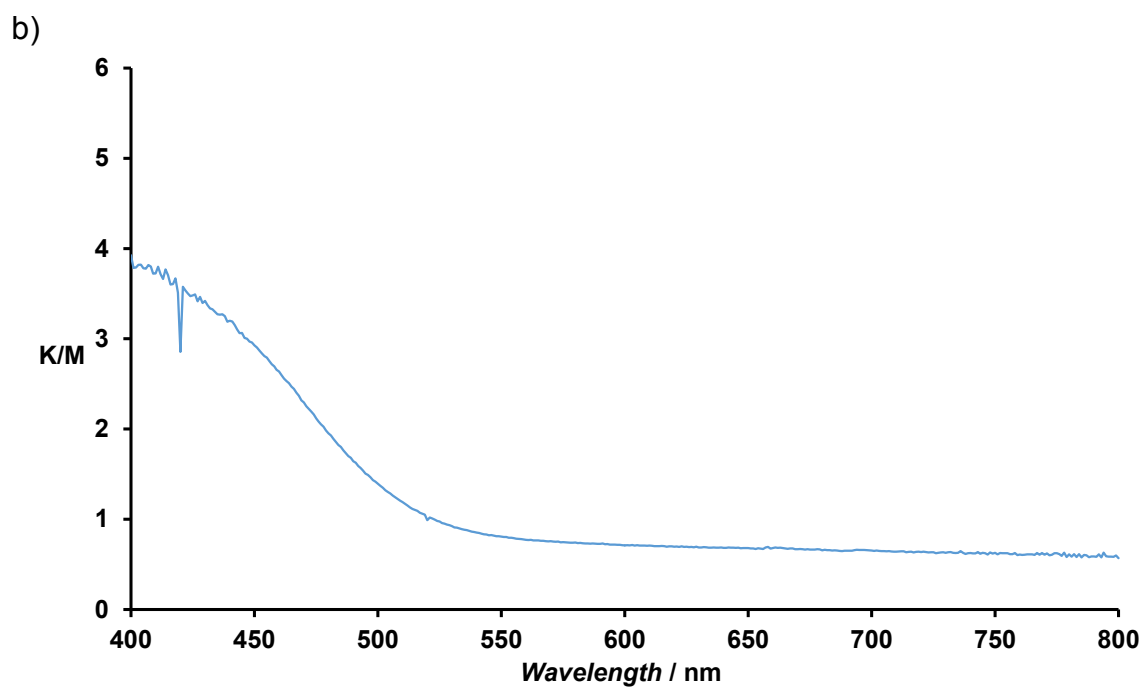
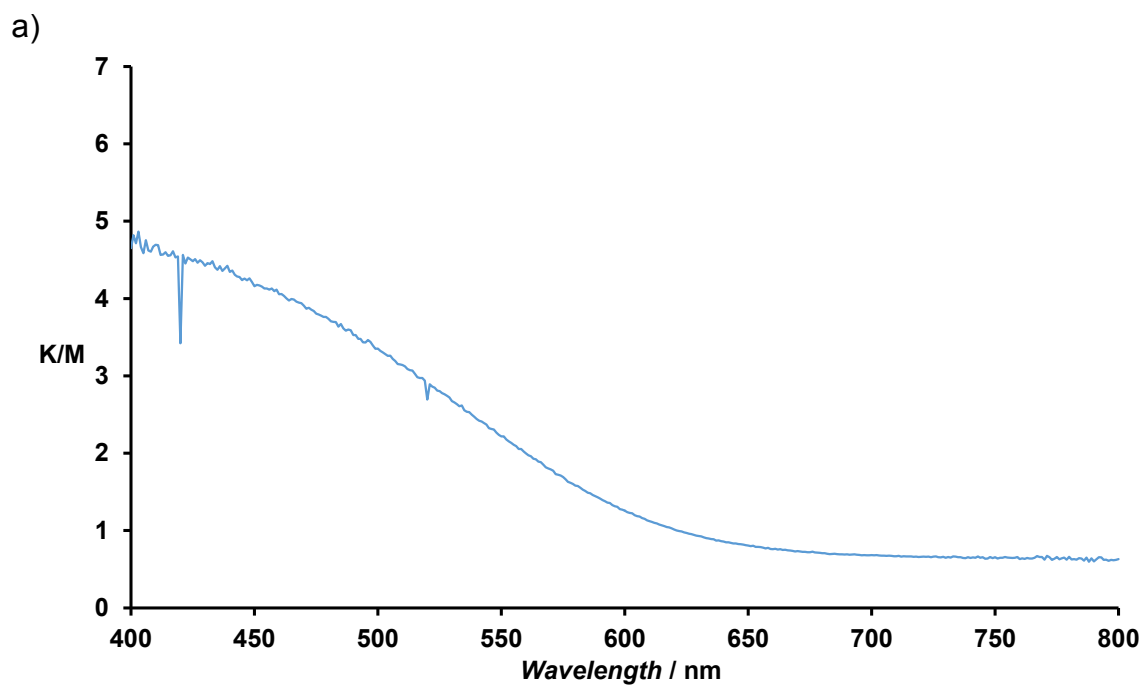
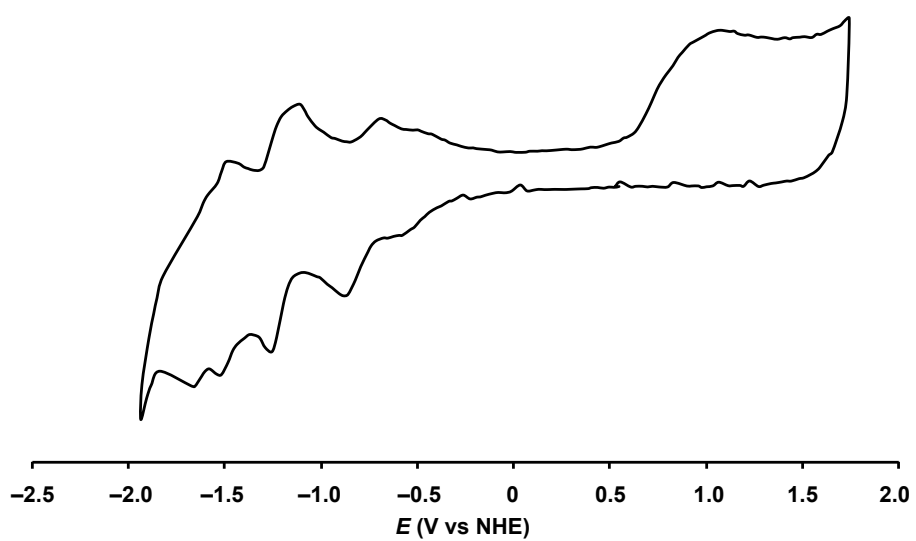


Fig. S14 UV/Vis diffuse reflectance spectra of a) **I** and b) **II**.

a)



b)

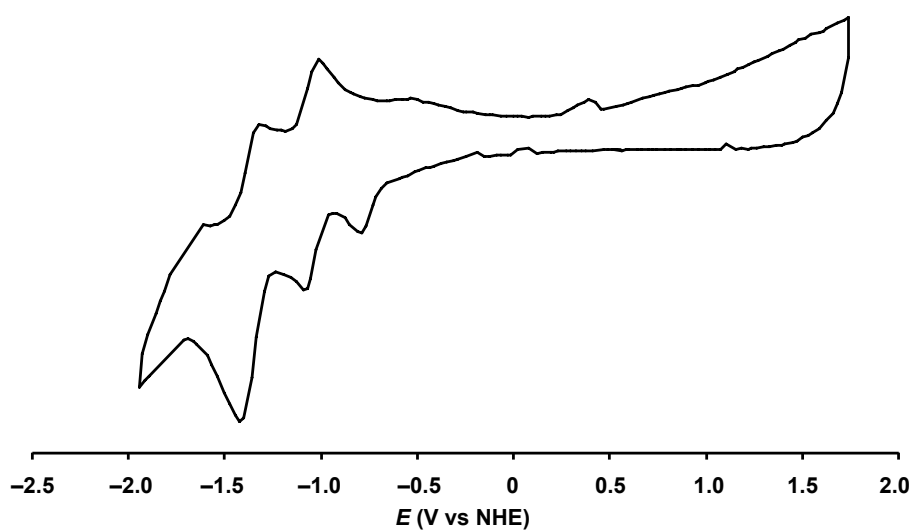


Fig. S15 Cyclic voltammogram of a) **I** and b) **II** (0.5 mM) in acetonitrile.