Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Metal-substituted tungstosulfates with Keggin structure: Synthesis and Characterization

Shinya Azuma,[a] Taiga Kadoguchi,[a] Yohei Eguchi,[a] Hikaru Hirabaru,[a] Hiromi Ota,[b] Masahiro Sadakane,[c] Kazumichi Yanagisawa,[d] Takuya Hasegawa,[e] Tadaharu Ueda[a,f,g,]*

a) Department of Applied Science, Faculty of Science, Kochi University, Kochi, 780-8520, Japan
b) Division of Instrumental Analysis, Department of Instrumental Analysis and Cryogenics, Advanced Science Research Center, Okayama University, Okayama, 700-8530, Japan
c) Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Hiroshima, Japan
d) Hydrothermal Reaction Center, Faculty of Science, Kochi University, Japan
e) Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai, Miyagi, 980-8577, Japan
f) Department of Marine Resources, Faculty of Agriculture and Marine Science, Kochi University, Nankoku, 783-8502, Japan
g) Center for Advanced Marine Core Research, Kochi University, Nankoku, 783-8520, Japan

Experimental

Preparation of (n-Bu$_4$N)$_4$H$_2$[SW$_{11}$O$_{39}$] (SW$_{11}$)

(n-Bu$_4$N)$_2$[SW$_{12}$O$_{40}$] (1.35 g) prepared by using the reported method,S1 was dissolved in 90 mL of acetone, and 0.9 mL of 1 M KHCO$_3$ was added. The formed white precipitation were separated by filtration, and then 40 mL of water containing 1.5 g of n-Bu$_4$NBr was added to the filtrate to generate a pale-yellow precipitate. If the precipitate was oily, it was washed with Et$_2$O under sonication to obtain a powdery precipitate. The precipitate was washed with water and ethanol and dried in air. The final crystalline product was obtained by recrystallization from dry acetone (Yield: 1.1 g). Anal. Calcd for (n-Bu$_4$N)$_4$H$_2$[SW$_{11}$O$_{39}$]: C 21.06, H 4.03, N 1.53, S 0.88%. Found; C 20.55, H 3.80, N 1.52, S 0.94%.

Preparation of the tetra-butylammonium salt of metal-substituted tungstosulfates, [SMW$_{11}$O$_{39}$]$^{n-}$ (M=Mn, Co, Ni, Cu)(SMW$_{11}$)

(n-Bu$_4$N)$_4$H$_2$[SW$_{11}$O$_{39}$] (0.948 g) was dissolved in 120 mL of acetone, and then 3.0 mL of 0.2 M metal-nitrate stock solution was added. After stirring the solution for 10 min, 70 mL of water containing 1.0 g of n-Bu$_4$NBr was added to afford a precipitate. It was collected by filtration and washed with a plenty of water and ethanol. Fine crystals were obtained by recrystallization from acetone. Yields: 0.92 g (M=Mn); 0.95 g (M=Co); 0.89 g (M=Ni); and 0.93 g (M=Cu). Calcd for (n-Bu$_4$N)$_4$[SMnW$_{11}$O$_{39}$]; C 20.74, H 3.97, N 1.51, S 0.86%. Found; C, 20.22, H 3.83, N 1.52, S 0.89%. Calcd for (n-Bu$_4$N)$_4$[SCoW$_{11}$O$_{39}$]; C 20.72, H 3.96, N 1.51, S 0.86%. Found; C 20.41, H 3.83, N 1.50, S 0.52%. Calcd for (n-Bu$_4$N)$_4$[SNiW$_{11}$O$_{39}$]; C 20.72, H 3.96, N 1.50, S 0.86%. Found; C, 20.61, H 3.85, N 1.48, S 0.87%. Calcd for (n-Bu$_4$N)$_4$[SCuW$_{11}$O$_{39}$]; C 20.69, H 3.96, N 1.50, S 0.86%. Found; C 20.90, H 3.68, N 1.47, S 0.87%.

Apparatus and reagents

X-ray single-crystal crystallographic data were collected with a Rigaku Saturn 724 diffractometer using multilayer mirror monochromated Mo-Kα radiation. The linear absorption coefficients, μ values, for Mo-Kα radiation are 116.904 cm^{-1} for SW$_{11}$, 112.191 cm^{-1} for SMnW$_{11}$, 112.728 cm^{-1} for SCoW$_{11}$, 114.980 cm^{-1} for SNiW$_{11}$ and 114.076 cm^{-1} for SCuW$_{11}$. An empirical absorption correction was applied, which resulted in transmission factors ranging from 0.203 to 0.311 for SW$_{11}$, from 0.202 to 0.291 for SMnW$_{11}$, from 0.363 to 0.508 for SCoW$_{11}$, from 0.265 to 0.317 for SCoW$_{11}$ and from 0.261 to 0.320 for SCuW$_{11}$. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[S2] and expanded using Fourier techniques. The cations and solvent molecules were omitted by the SQUEEZE procedure[S3] because it was not important to elucidate the interaction between the POMs and the tetra-alkyl ammonium cations.[17] The final cycle of full-matrix least-squares refinement[S4] on F^2 was based on 649 observed reflections for SW$_{11}$, 668 observed reflections for SMnW$_{11}$, 669 observed reflections for SCoW$_{11}$, 668 observed reflections for SNiW$_{11}$, and 675 observed reflections for SCuW$_{11}$, and 19 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.0934$ for SW$_{11}$, 0.0726 for SMnW$_{11}$, 0.0417 for SCoW$_{11}$, 0.0489 for SNiW$_{11}$, and 0.0362 for SCuW$_{11}$

$wR_2=[\Sigma(w(F_o^2-F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2} = 0.2189$ for SW$_{11}$, 0.1755 for SMnW$_{11}$, 0.1056 for SCoW$_{11}$, 0.1151 for SNiW$_{11}$, and 0.0866 for SCuW$_{11}$

The goodness of fits[S5] were 1.28 for SW$_{11}$, 1.21 for SMnW$_{11}$, 1.08 for SCoW$_{11}$, 1.13 for SNiW$_{11}$, and 1.03 for SCuW$_{11}$. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.64 and -0.90 e$^-$/Å^3 for SW$_{11}$, 1.06 and -0.76 e$^-$/Å^3 for SMnW$_{11}$, 1.69 and -1.23 e$^-$/Å^3 for SCoW$_{11}$, 1.85 and -1.18 e$^-$/Å^3 for SNiW$_{11}$ and 0.96 and -0.75 e$^-$/Å^3 for SCuW$_{11}$.

Neutral atom scattering factors were taken from the International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4 5.[S6] Anomalous dispersion effects were included in Fcalc;[S7] the values for Df' and Df" were those of Creagh and McAuley.[S8] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[S9] All calculations were performed using the Rigaku Corporation

CrystalStructure9 crystallographic software package except for refinement, which was performed using SHELXL Version 2016/6SHELXL97.[S10]

Elemental analyses was carried out with PERKIN ELMER Series II CHNS/O Analyzer 2400. ESI-MS spectra were obtained in CH_3CN in anion mode with a Thermo Fisher Scientific LTQ Orbitrap XL instrument, and ionization was achieved by applying 5 kV. Spectrophotometric measurements were carried out by using a Jasco FT/IR-4100 IR spectrometer, a Horiba-Jobin Yvon HR-800 instrument with a 514.5 nm Ar laser for excitation for Raman, and a Jasco V-670 for UV-Vis spectrophotometry.

Voltammetric measurements were carried out with a BAS 50 W (Bioanalytical Systems, BAS) electrochemical workstation. A standard three-electrode arrangement was employed: a glassy carbon disk electrode with a surface area of 0.071 cm^2 was used as working electrode, platinum wire was used as the counter electrode, and Ag/Ag^+ (0.01 M $AgNO_3$ in CH_3CN) was used as the reference electrode. The silver wire was put in 0.01 M $AgNO_3$ containing CH_3CN in a double-jacketed system separated by sintered glass. Unless otherwise stated, the scan rate for voltammetric experiments was 100 mV s^{-1}. The measured potential versus Ag/Ag^+ was converted to the Fc/Fc^+ (Fc = ferrocene) scale using data derived from voltammograms of the oxidation of ferrocene. Prior to each measurement, the glassy carbon electrode (GCE) was polished with an aqueous 0.1-µm diamond slurry and washed with distilled water. The sample solution was always purged with nitrogen or argon gas to remove dissolved oxygen. All electrochemical measurements were made at 25.0±0.2ºC.

Tetrabutylammonium hexafluorophosphate, $[n\text{-}Bu_4N][PF_6]$, recrystallized at least twice from ethanol, was used as the electrolyte in the electrochemical experiments. Acetonitrile (CH_3CN) of LC-MS grade were purchased from WAKO and used as received from the manufacturer for ESI-MS and electrochemical measurements. Other reagents were of analytical grade and were used as received.

References and notes

(S1) Himeno, S.; Takamoto, M.; Hoshiba, M.; Higuchi, A.; Hashimoto, M., Preparation and characterization of an α-Keggin-type $[SW_{12}O_{40}]^{2-}$ complex. *Bull. Chem. Soc. Jpn.* **2004,** *77*, 519-524.

(S2) Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. Siliqi, D. and Spagna R. *J. Appl. Cryst.* 2007, 40, 609-613.

(S3) Spek, A. L., *Acta Cryst.*, **2009**, D65, 148-155.

(S4) Least Squares function minimized (SHELXL97): $\Sigma w(F_O^2-F_C^2)^2$ where w = Least Squares weights.

(S5) Goodness of fit is defined as: $[\Sigma w(F_O^2-F_C^2)^2/(N_O-N_V)]^{1/2}$ where: N_O= number of observations; N_V= number of variables

(S6) International Tables for Crystallography, Vol. C. Ed. A.J.C. Wilson, Kluwer Academic Publishers, Dordrecht, Netherlands, Table 6.1.1.4, 1992, pp. 572.

(S7) Ibers, J. A. & Hamilton, W. C.; *Acta Cryst.*, 1664, 17, 781.

(S8) Creagh, D. C. & McAuley, W.J.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, 1992, p. 219-222.

(S9) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, 1992, p. 200-206.

(S10) Sheldrick, G. M. *Acta Cryst.* 2008, A64, 112-122.

Table S1 Crystallographic data for $[SW_{11}O_{39}]^{6-}$, $[SMnW_{11}O_{39}]^{4-}$, $[SCoW_{11}O_{39}]^{4-}$, $[SNiW_{11}O_{39}]^{4-}$ and $[SCuW_{11}O_{39}]^{4-}$.

Formula	$SW_{11}O_{39}$	$SMnW_{11}O_{39}$	$SCoW_{11}O_{39}$	$SNiW_{11}O_{39}$	$SCuW_{11}O_{39}$
FW(g mol^{-1})	2678.39	2733.32	2737.32	2737.09	2741.93
Crystal system	cubic	cubic	cubic	cubic	cubic
Space group	$Im\bar{3}m$ (229)	$Im\bar{3}m$ (229)	$Im\bar{3}m$ (229)	$Im\bar{3}m$ (229)	$Im\bar{3}m$ (229)
a(Å)	17.565	17.864	17.854	17.747	17.805
V(Å^3)	5419(5)	5701(9)	5691(8)	5590(8)	5645(8)
Z	2	2	2	2	2
d_{calcd} g/cm^3	1.641	1.592	1.597	1.626	1.574
No. observations (all data)	42711	43310	43956	43725	43579
GOF	1.282	1.211	1.084	1.134	1.030
final R indices(I>2.00σ(I))^a	R_1=0.0934 wR_2=0.2188	R_1=0.0726 wR_2=0.1739	R_1=0.0417 wR_2=0.1054	R_1=0.0489 wR_2=0.1147	R_1=0.0362 wR_2=0.0859
final R indices(all data)^b	R_1=0.0931 wR_2=0.2189	R_1=0.0753 wR_2=0.1755	R_1=0.0419 wR_2=0.1056	R_1=0.0495 wR_2=0.1151	R_1=0.0373 wR_2=0.0866

$^aR_1=\sum ||F_o| - |F_c||/ \sum |F_o|$ $(I > 2.00\ \sigma (I))$. $^bwR_2 = [\sum (w(F_o^2 - F_c^2)^2)/ \sum w(F_o^2)^2]^{1/2}$.

Table S2 Observed and calculated ionic molecular weights per anion charge (m/z) of POMs in ESI-MS spectra.

POMs	Calculated m/z	Observed m/z
$H[SW_{11}O_{38}]^{3-}$	887.4182	887.4181
$H[SMn^{II}W_{11}O_{39}]^{3-}$	911.0606	911.0604
$H[SCo^{II}W_{11}O_{39}]^{3-}$	912.3923	912.3921
$H[SNi^{II}W_{11}O_{39}]^{3-}$	912.7265	912.7259
$[SCu^{III}W_{11}O_{39}]^{3-}$	914.0556	914.0547

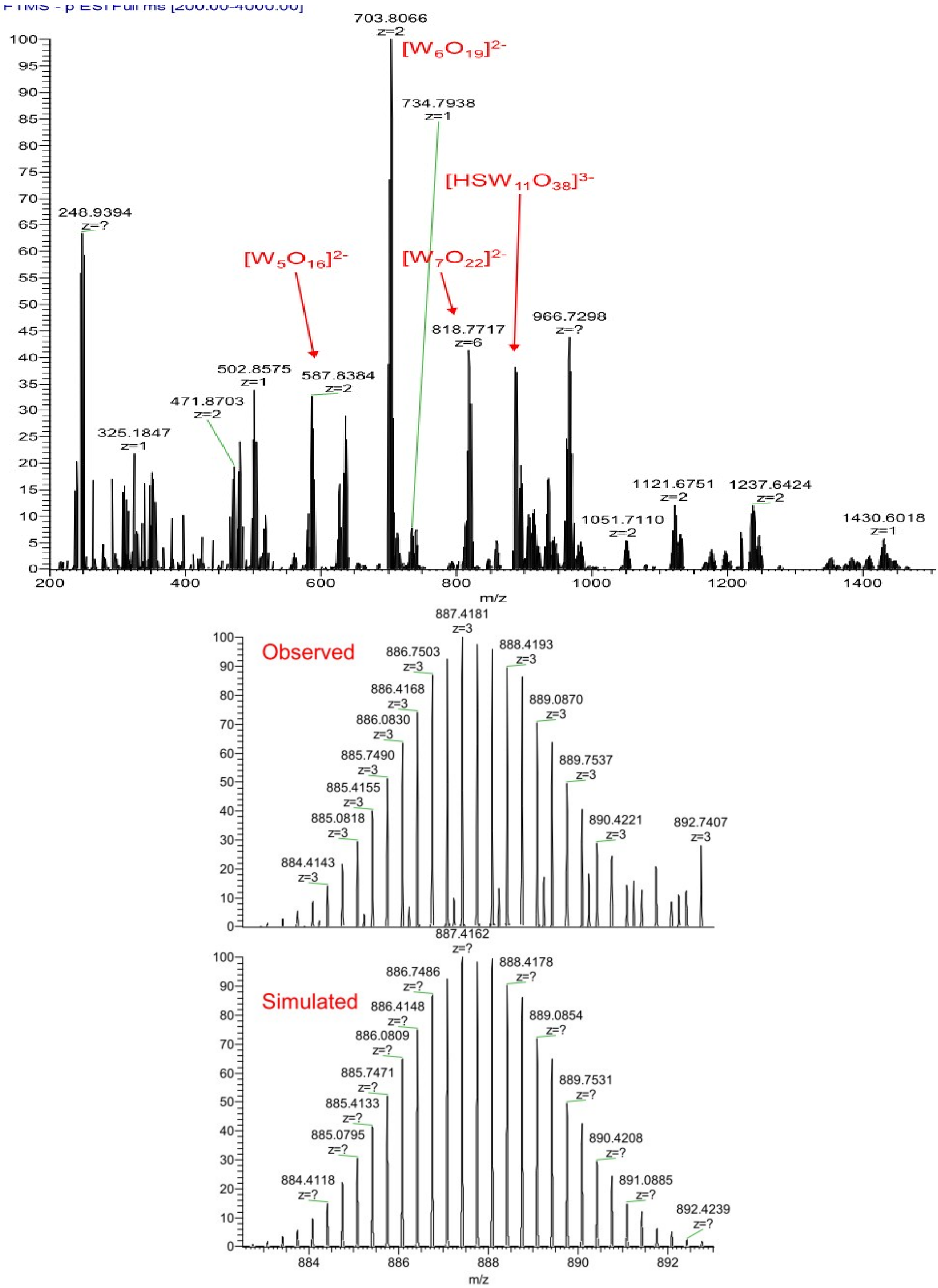

Figure S1 ESI-MS spectra of $(Bu_4N)_4H_2[SW_{11}O_{39}]$ dissolved in CH_3CN. (top) Spectrum between *m/z* of 200 and 1500 and (bottom) expansion of the profile assignable to $[HSW_{11}O_{38}]^{3-}$.

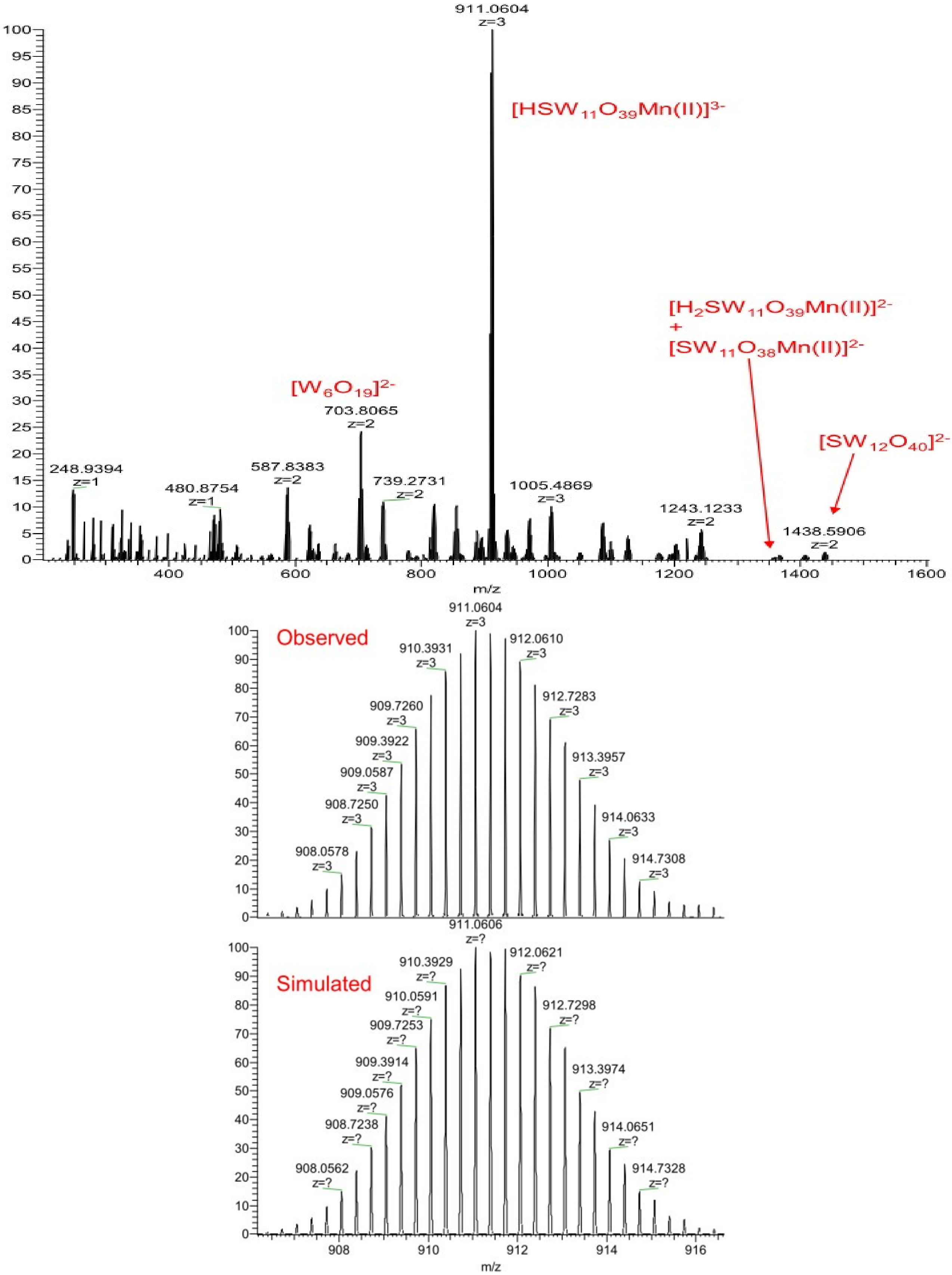

Figure S2 ESI-MS spectra of (Bu$_4$N)$_4$[SMnW$_{11}$O$_{39}$] dissolved in CH$_3$CN. (top) Spectrum between *m/z* of 200 and 1600 and (bottom) expansion of the profile assignable to [HSMnW$_{11}$O$_{39}$]$^{3-}$.

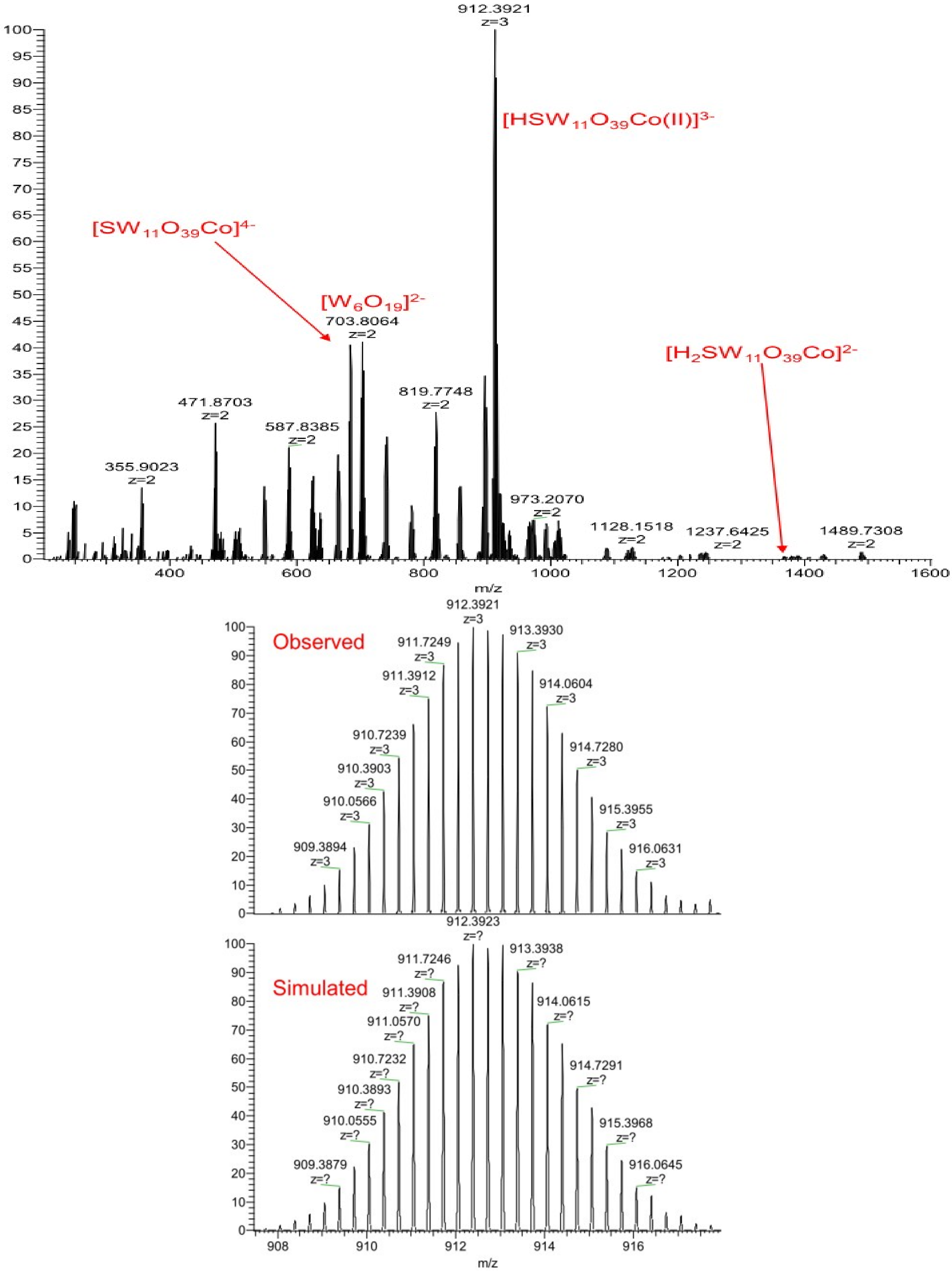

Figure S3 ESI-MS spectra of $(Bu_4N)_4[SCoW_{11}O_{39}]$ dissolved in CH_3CN. (top) Spectrum between *m/z* of 200 and 1600 and (bottom) expansion of the profile assignable to $[HSCoW_{11}O_{39}]^{3-}$.

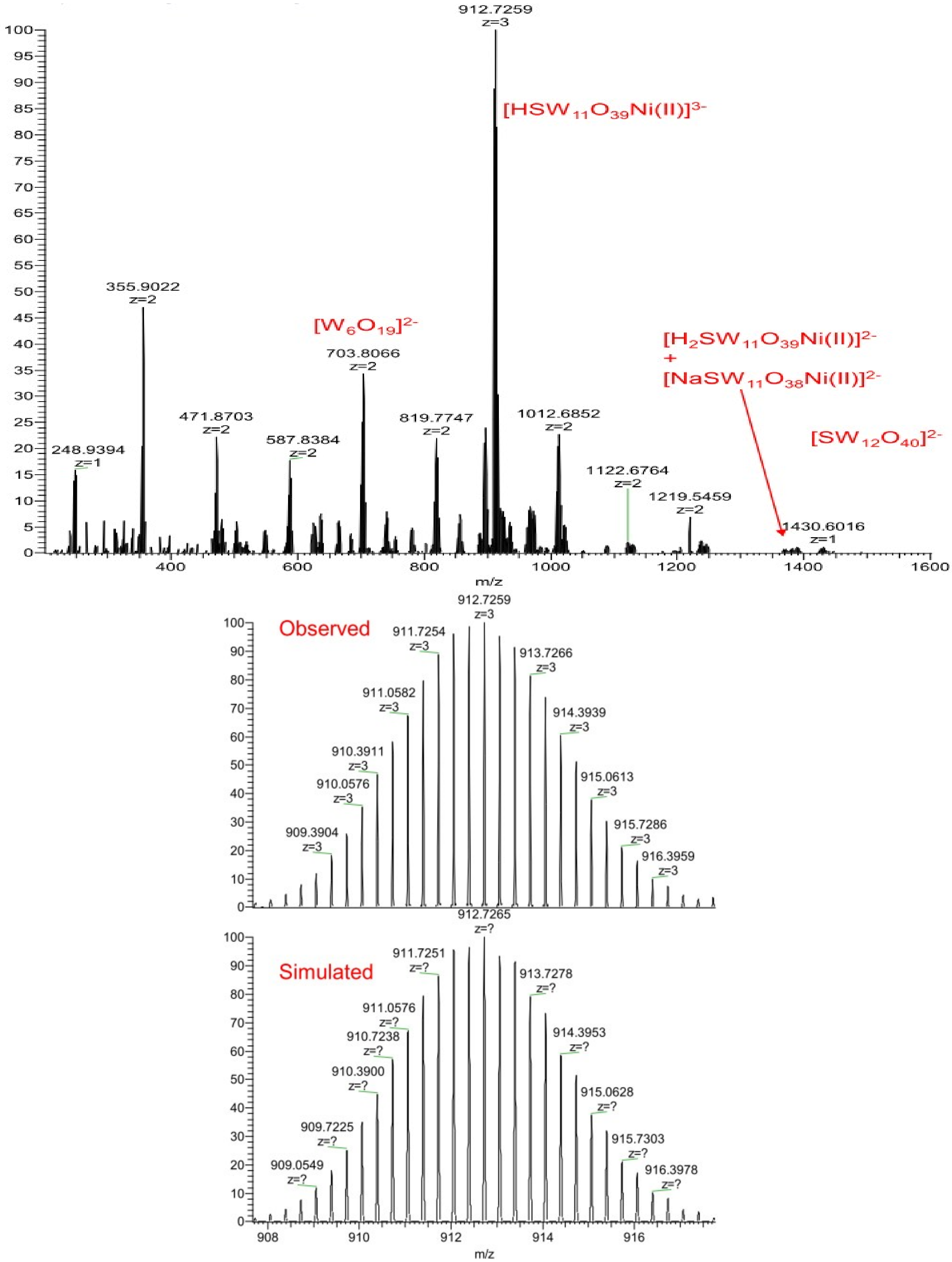

Figure S4 ESI-MS spectra of $(Bu_4N)_4[SNiW_{11}O_{39}]$ dissolved in CH_3CN. (top) Spectrum between *m/z* of 200 and 1600 and (bottom) expansion of the profile assignable to $[HSNiW_{11}O_{39}]^{3-}$.

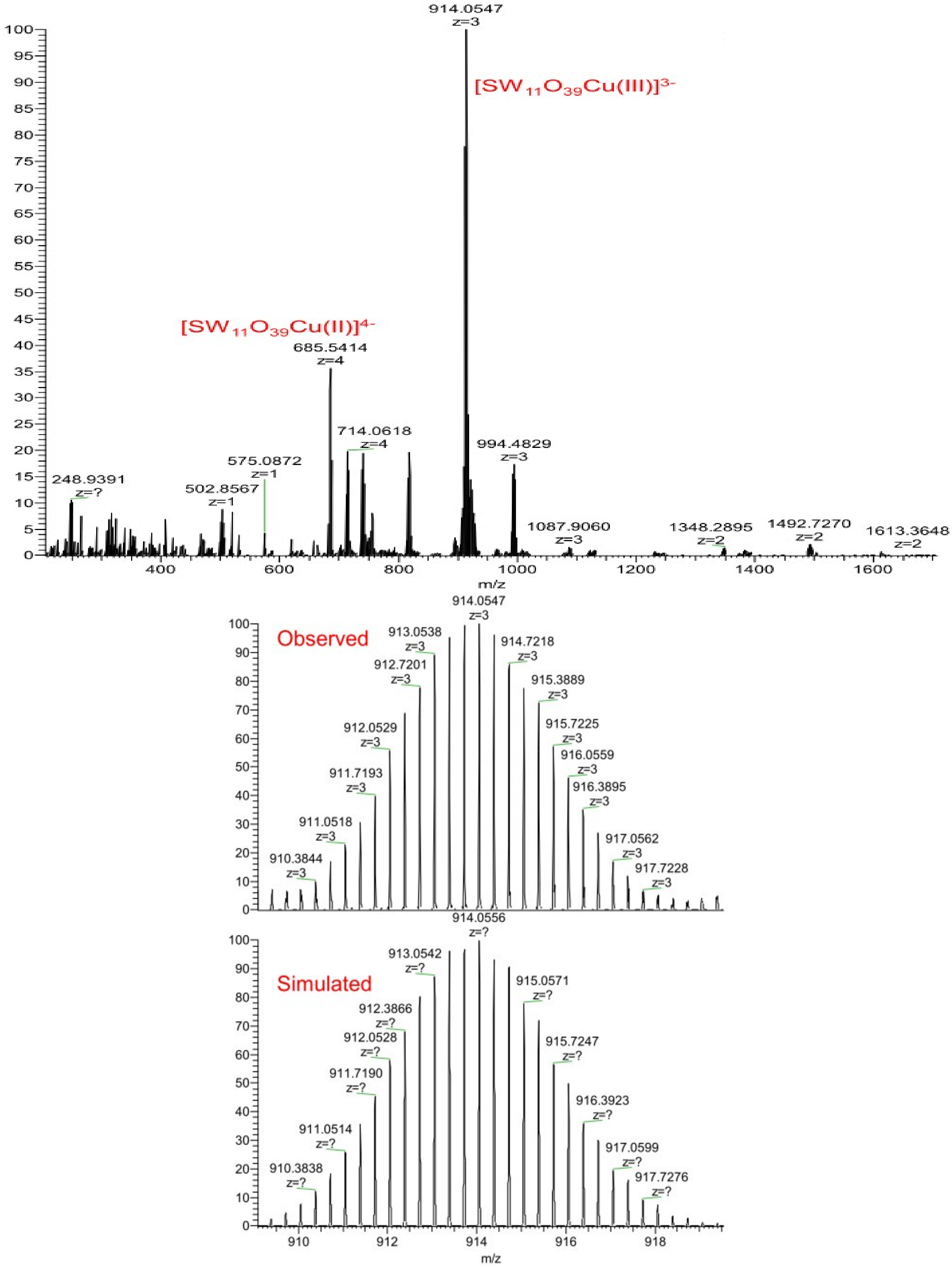

Figure S5 ESI-MS spectra of $(Bu_4N)_4[SCuW_{11}O_{39}]$ dissolved in CH_3CN. (top) Spectrum between *m/z* of 200 and 1600 and (bottom) expansion of the profile assignable to $[SCuW_{11}O_{39}]^{3-}$.

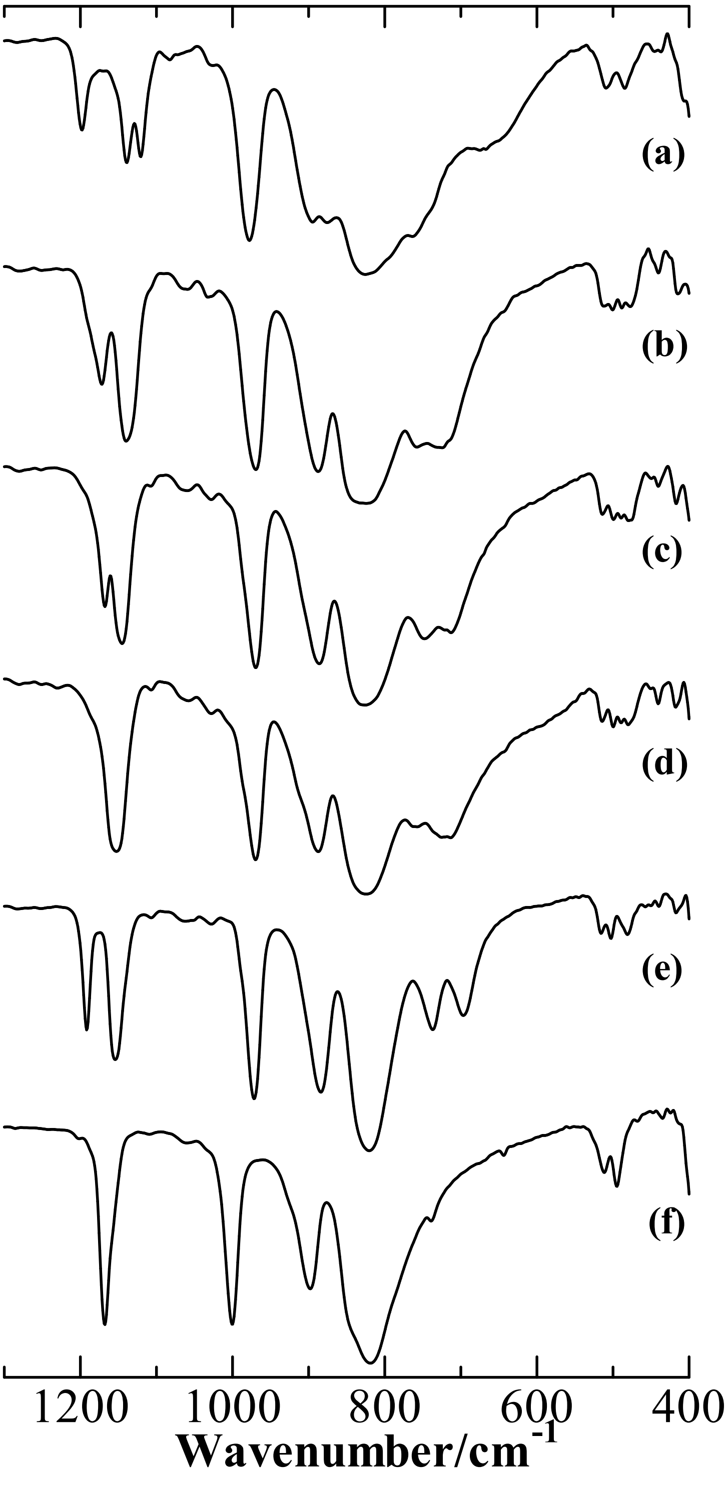

Figure S6 IR spectra of the tetra-butyl ammonium salts of (a) $[SW_{11}O_{39}]^{6-}$, (b) $[SMnW_{11}O_{39}]^{4-}$, (c) $[SCoW_{11}O_{39}]^{4-}$, (d) $[SNiW_{11}O_{39}]^{4-}$, (e) $[SCuW_{11}O_{39}]^{4-}$ and (f) $[SW_{12}O_{40}]^{2-}$.

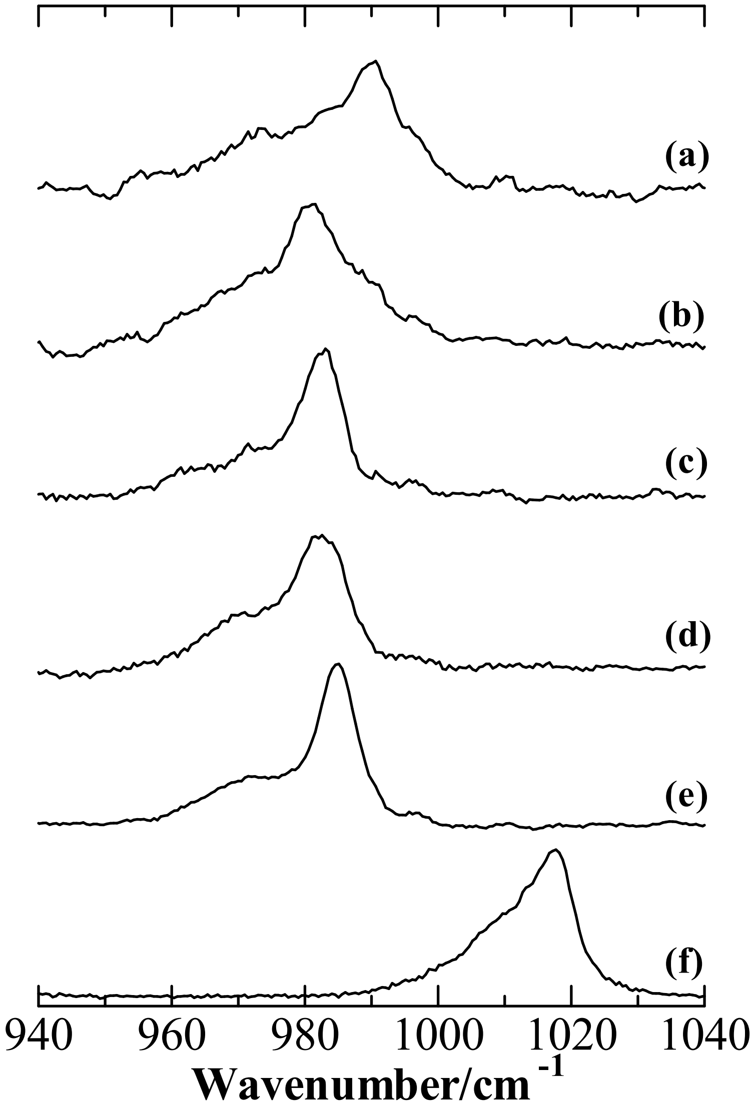

Figure S7 Raman spectra of the tetra-butyl ammonium salts of (a) $[SW_{11}O_{39}]^{6-}$, (b) $[SMnW_{11}O_{39}]^{4-}$, (c) $[SCoW_{11}O_{39}]^{4-}$, (d) $[SNiW_{11}O_{39}]^{4-}$, (e) $[SCuW_{11}O_{39}]^{4-}$ and (f) $[SW_{12}O_{40}]^{2-}$.

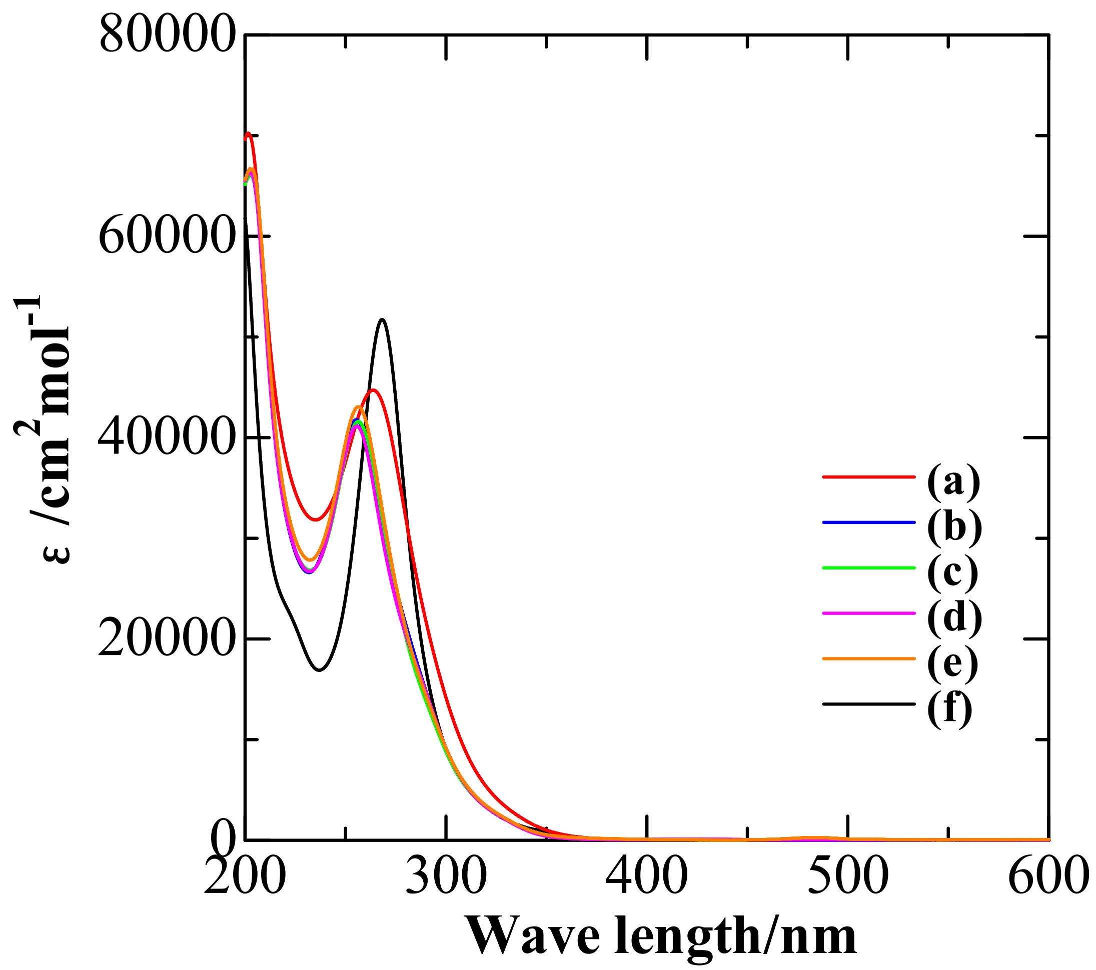

Figure S8 UV-Vis spectra of (a) $[SW_{11}O_{39}]^{6-}$, (b) $[SMnW_{11}O_{39}]^{4-}$, (c) $[SCoW_{11}O_{39}]^{4-}$, (d) $[SNiW_{11}O_{39}]^{4-}$, and (e) $[SCuW_{11}O_{39}]^{4-}$ in CH_3CN and (f) $[SW_{12}O_{40}]^{2-}$ in acetone.