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Supporting Information

High-nuclearity isopolyoxotungstate based manganese cluster: one-pot synthesis and step-by-step assembly

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Section 2 Results and Discussion

Experimental Procedures

Experimental details.

General methods and materials. The reagents were commercially purchased and used without further purification. Elemental analyses of Na, Mn, W were analyzed on were performed on a Perkin-Elmer Optima 2000 ICP-OES spectrometer. The IR spectra were obtained in KBr pellets with a Nicolet FT-IR 360 spectrometer over the range of 4000–400 cm^{-1}. Magnetic susceptibility measurements were obtained by the use of a Quantum Design SQUID (MPMS-XL7) magnetometer (0.1 Tesla) at a temperature ranging from 1.8 to 300 K. Electrospray Ionization Mass Spectrometry (ESI-MS) was performed using a Triple TOF 4600-1 mass spectrometer. All samples were prepared as described in the following and injected directly at a flow rate of 5 μL min^{-1} using a syringe pump. All spectra were collected in negative and positive mode and analyzed using the PeakView software.

STM sample preparation and characterization: All the solutions were prepared by dissolving the chemicals in heptanoic acid with the concentration less than 10^{-4} M. A droplet of TCDB solution (0.1 μL) was first deposited onto the freshly cleaved highly oriented pyrolytic graphite (HOPG, grade ZYA, NTMDT, Russia) surface for STM characterization of the TCDB template network. Subsequently, a droplet of 1 solution (0.1 μL) was added to the surface for characterization of the host-guest structure. The samples were characterized at the liquid-solid interface using a Nanoscope IIIA system (Bruker, USA) under ambient conditions. The STM tips were mechanically cut from Pt/Ir (80/20) wires. All the images were captured in constant-current mode and specific tunneling conditions are noted in the figure captions.

All electrochemical experiments were conducted on a CH Instrument (660E) electrochemical station in a standard three electrode cell at room temperature. A glassy carbon electrode (diameter = 5mm), an Ag/AgCl (3.5 M KCl), and a Pt wire were used as the working electrode, reference and counter electrode, respectively. The cyclic voltammogram (CV) curve of compound **1** (1 mM) in distilled water (supporting electrolyte 0.1 M Na_2SO_4) was tested in the range of -1 – +1.35V vs Ag/AgCl with a scan rate of 100 mV s^{-1}.

Crystal data for $Na_8H_{32}[\{Mn^{IV}_{24}Mn^{III}_{12}O_{28}(H_2O)_{23}\}_2(W_{24}O_{120})_2]\cdot 66H_2O$ (**1a**): A reddish-black plate-like crystal of **1a** with dimensions 0.48 × 0.18 × 0.07 mm^3 was mounted on a Hampton cryo-loop for indexing and intensity data collection at 296 K on Bruker Apex-II CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å). Of the 64134 reflection collected ($2\theta_{max}$ = 50.00, 99.4% complete), 43555 were unique (R_{int} = 0.0713). Routine Lorentz polarization and empirical absorption correction were applied. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 with SHELXTL-2014 and olex2 program package. No hydrogen atoms could be located from the difference Fourier map. Further details on the crystal structure investigations may be obtained from https://www.ccdc.cam.ac.uk/structures/ (CCDC No. 1574960).

Preparation of sol.Mn:

$Mn(CH_3COO)_2·4H_2O$ (1.00 g, 4.08 mmol) was dissolved in 10mL 60% (v/v) CH_3COOH solution. After dissolution, $KMnO_4$ (0.25 g, 1.58 mmol) was added to the solution, and the mixture was vigorously stirred for one hour.

Preparation of 1:

In a 50 mL beaker, a sample of $Na_2WO_4·2H_2O$ (1.0 g) was dissolved in 30 mL H_2O. The pH of the solution was then adjusted to about 5.5 with **sol.Mn**. Then the dark orange/brown mixture was heated to 90 °C for 1 hour, cooled to room temperature and then filtered. The colorless, block-shaped crystals of para-dodecatungstate ($[H_2W_{12}O_{42}]^{10-}$, which appeared the following day, were filtered off. In the filtrate reddish-black, plate-like crystals formed after approximately one week. The orange crystals of $Na_8MnW_6O_{24}·xH_2O$ appeared before the mother liquid dried up.

Typically yields of **1**: *ca*. 6 % based on Mn. IR (KBr pellet, υ/cm^{-1}): 3424 (br/m), 1629 (m), 943 (w), 826 (m), 682 (s). Elemental analysis (%) for **1**, calcd: Na: 0.94, Mn: 20.27, W: 45.22; found: Na: 0.89, Mn: 20.35, W: 45.34.

Results and Discussion

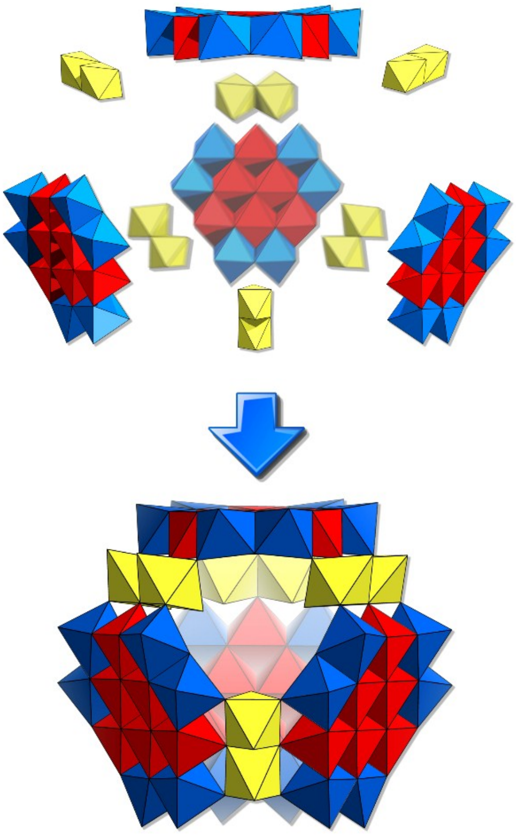


Fig. S1. Scheme showing the key building blocks of the $\mathbf{Mn_{36}W_{24}}$ cage in **1**: four planar $\mathbf{Mn_6}$ fragments, twelve $\mathbf{W_2}$ groups, and six $\mathbf{Mn_2}$ groups. The cage-like moiety $\mathbf{Mn_{36}W_{24}}$ could hence be regarded as being composed of four planar $\{Mn^{IV}_6W_6\}$ fragments connected by six $\mathbf{Mn_2}$ linkers. Color code of the MO_6 octahedra: Mn^{IV}: red; Mn^{III}: yellow; W: blue.

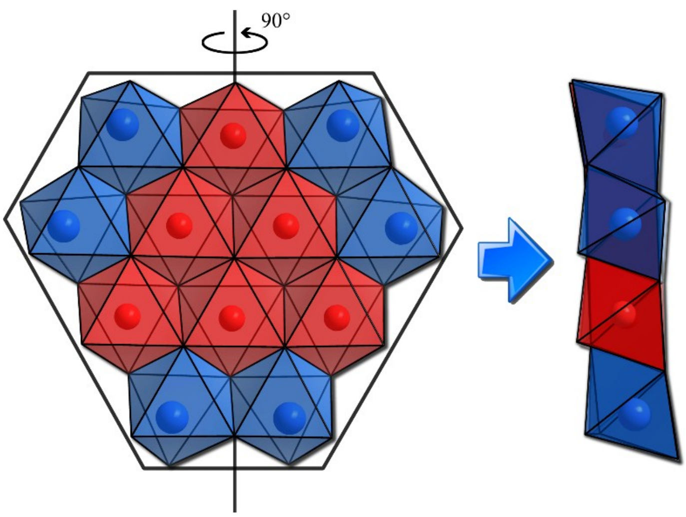


Fig. S2. Three $\mathbf{W_2}$ units attached to a triangular $\mathbf{Mn_6}$ unit, leading to a larger, planar building block, forming the sides of the $\mathbf{Mn_{36}W_{24}}$ cage. Color code of the MO_6 octahedra: Mn^{IV}: red; W: blue.

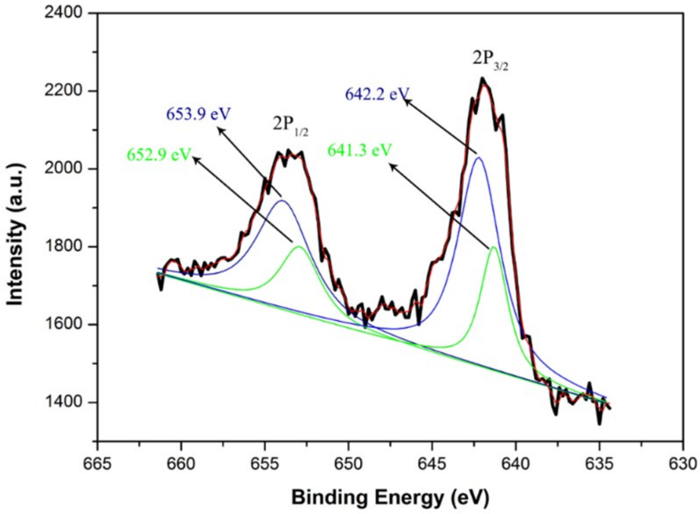
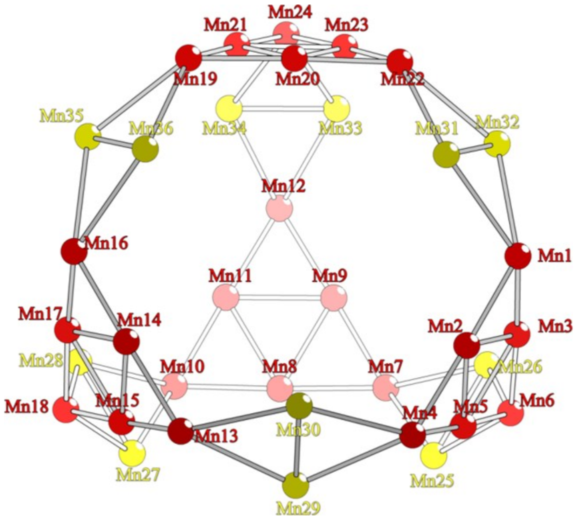


Fig. S3. XPS spectrum of **1** showing Mn 2P$_{1/2}$ and 2P$_{3/2}$.

	BVS value			
	Mn(II)	Mn(III)	Mn(IV)	Mn(VII)
Mn1	4.61	4.25	**4.17**	4.61
Mn2	4.42	4.07	**4.00**	4.42
Mn3	4.41	4.07	**3.99**	4.41
Mn4	4.42	4.08	**4.00**	4.42
Mn5	4.27	3.94	**3.87**	4.27
Mn6	4.49	4.14	**4.06**	4.49
Mn7	4.35	4.01	**3.93**	4.35
Mn8	4.49	4.14	**4.06**	4.49
Mn9	4.60	4.24	**4.16**	4.60
Mn10	4.29	3.95	**3.88**	4.29
Mn11	4.39	4.04	**3.97**	4.39
Mn12	4.45	4.10	**4.02**	4.45
Mn13	4.45	4.11	**4.03**	4.45
Mn14	4.41	4.07	**3.99**	4.41
Mn15	4.42	4.08	**4.00**	4.42
Mn16	4.49	4.14	**4.06**	4.49
Mn17	4.43	4.08	**4.01**	4.43
Mn18	4.55	4.19	**4.12**	4.55
Mn19	4.41	4.06	**3.99**	4.41
Mn20	4.35	4.01	**3.94**	4.35
Mn21	4.40	4.06	**3.98**	4.40
Mn22	4.45	4.10	**4.03**	4.45
Mn23	4.27	3.93	**3.86**	4.27
Mn24	4.60	4.24	**4.16**	4.60
Mn25	3.32	**3.06**	3.00	3.32
Mn26	3.30	**3.04**	2.98	3.30
Mn27	3.35	**3.08**	3.03	3.35

Fig. S4 / Table S1. Bond valence sum (BVS) values (calculated according to N. E. Brese, M. O'Keeffe, *Acta Crystallogr. Sect. B* **1991**, *47*, 192) for the Mn centers in **1**. The assigned oxidation states are highlighted in bold with a colored background (red: Mn^{IV}, yellow: Mn^{III}).



Mn28	3.28	**3.02**	2.97	3.28
Mn29	3.31	**3.05**	3.00	3.31
Mn30	3.16	**2.92**	2.86	3.16
Mn31	3.31	**3.05**	2.99	3.31
Mn32	3.36	**3.10**	3.04	3.36
Mn33	3.24	**2.98**	2.93	3.24
Mn34	3.27	**3.01**	2.96	3.27
Mn35	3.32	**3.06**	3.00	3.32
Mn36	3.31	**3.06**	3.00	3.31

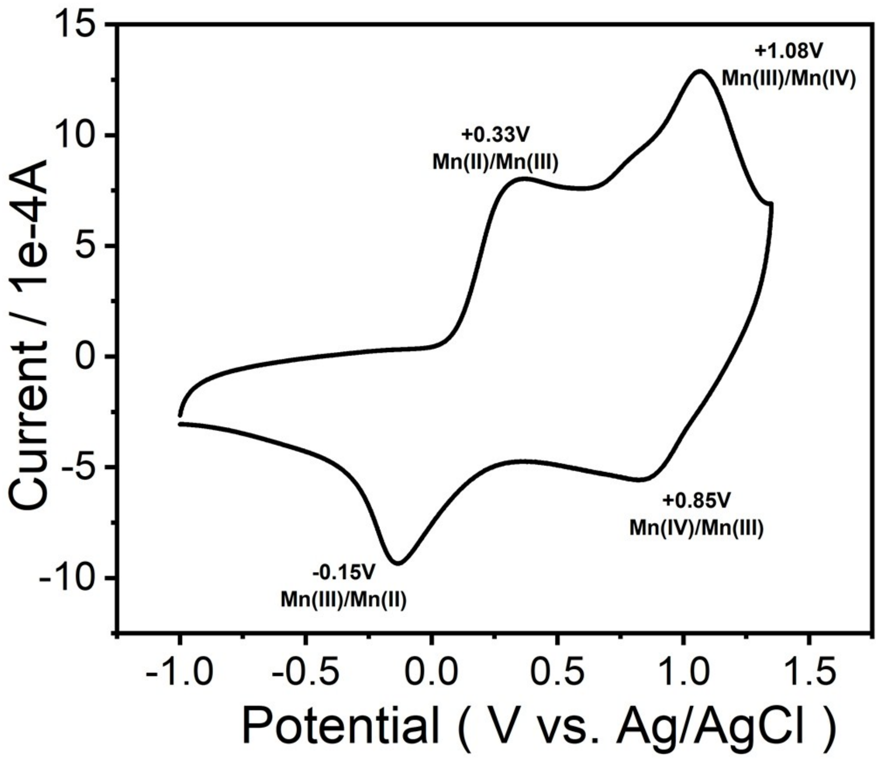


Fig. S5 Cyclic voltammogram of 1 mM $\mathbf{Mn_{72}W_{48}}$ (used supporting electrolyte 0.1 M Na2SO_4) , scan rate was 100 mV/s

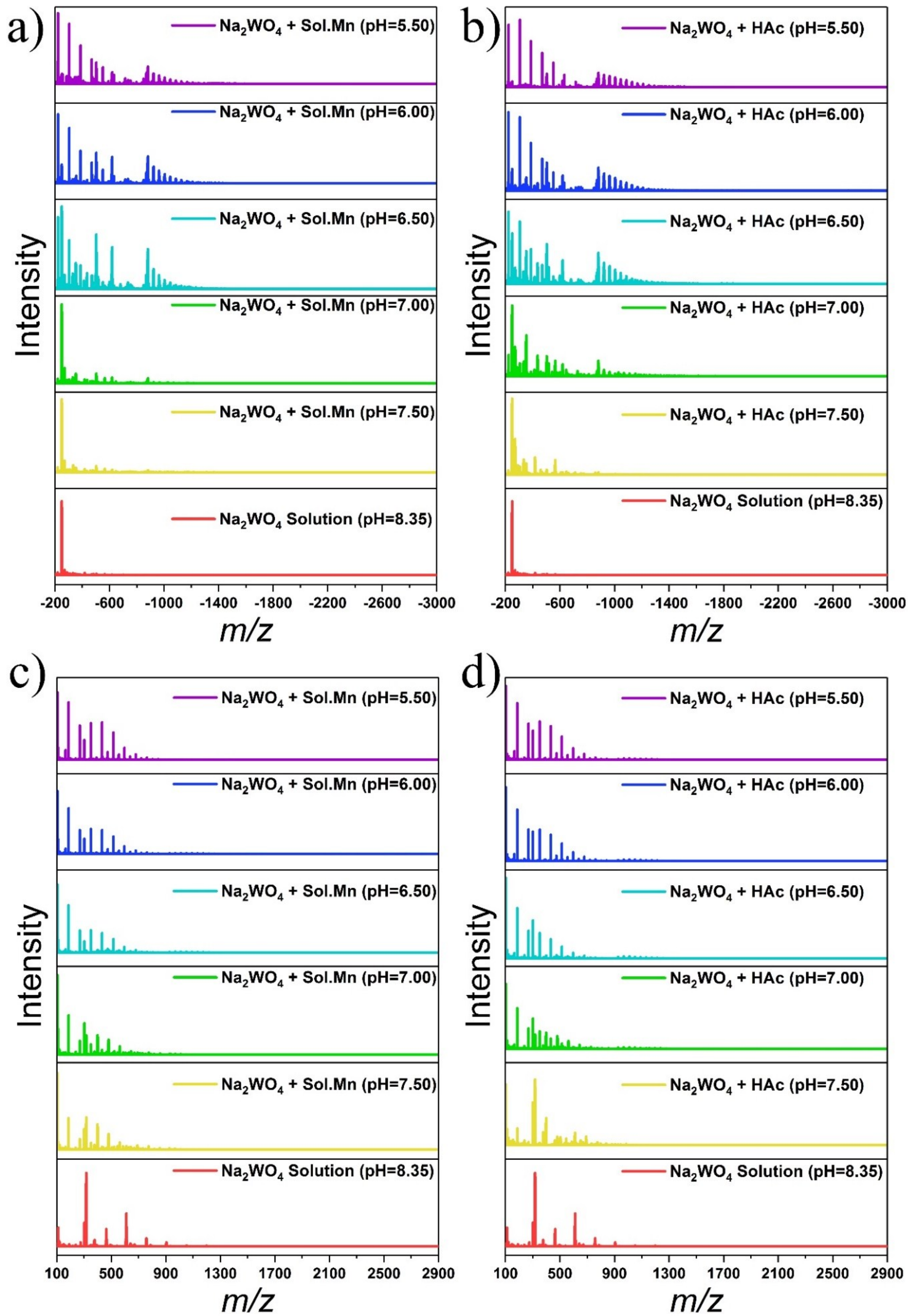


Fig. S6 Negative and positive mode of ESI-MS spectra of **sol.W-Mn** (a, c) and **sol.W-HAc** (b, d).

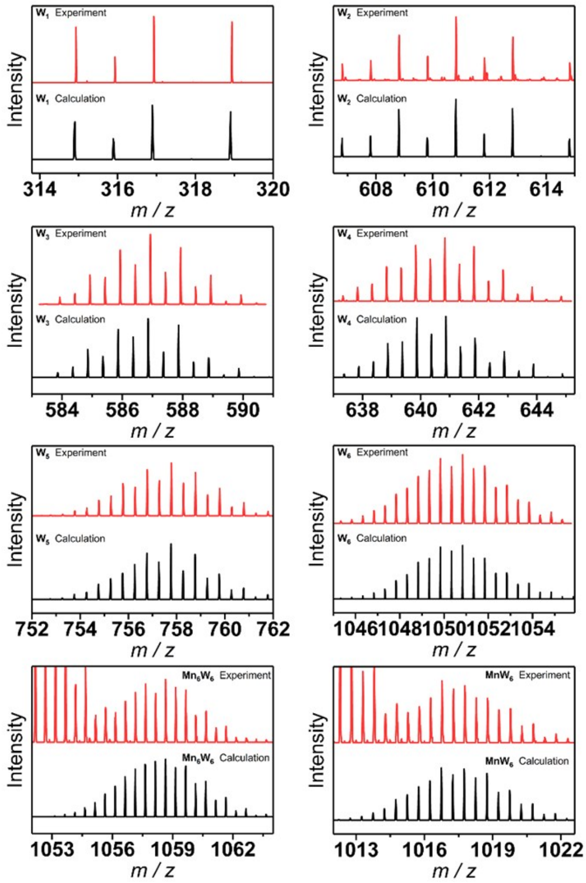


Fig. S7 Selected experimental (red) and simulated (black) mass spectra of the isotopic envelopes for **sol.W-Mn** in positive mode.

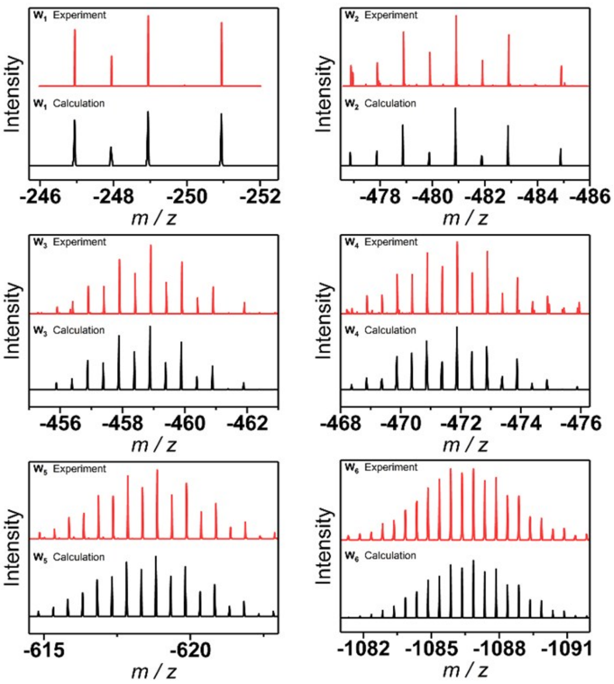


Fig. S8 Selected experimental (red) and simulated (black) mass spectra of the isotopic envelopes for **sol.W-Mn** in negative mode.

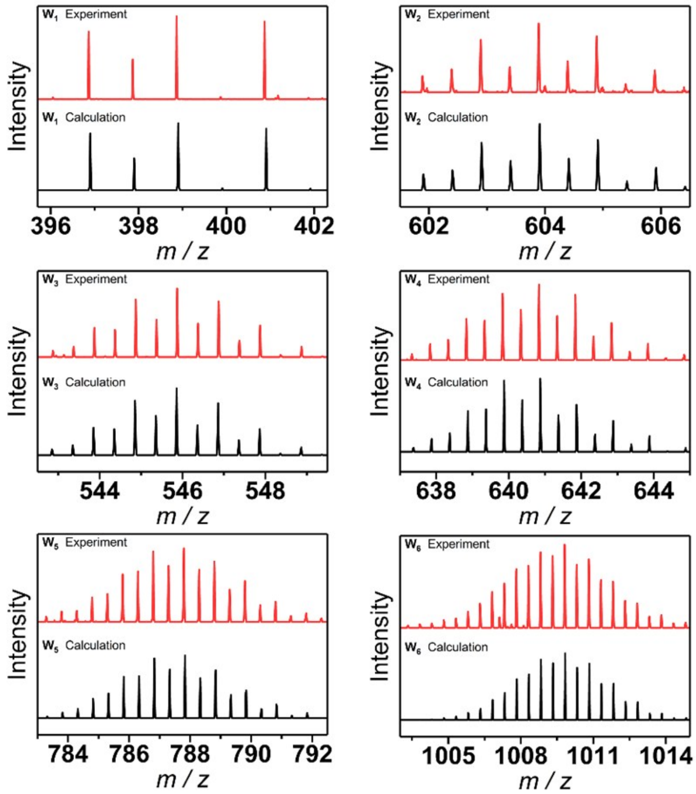


Fig. S9 Selected experimental (red) and simulated (black) mass spectra of the isotopic envelopes for **sol.W-HAc** in positive mode.

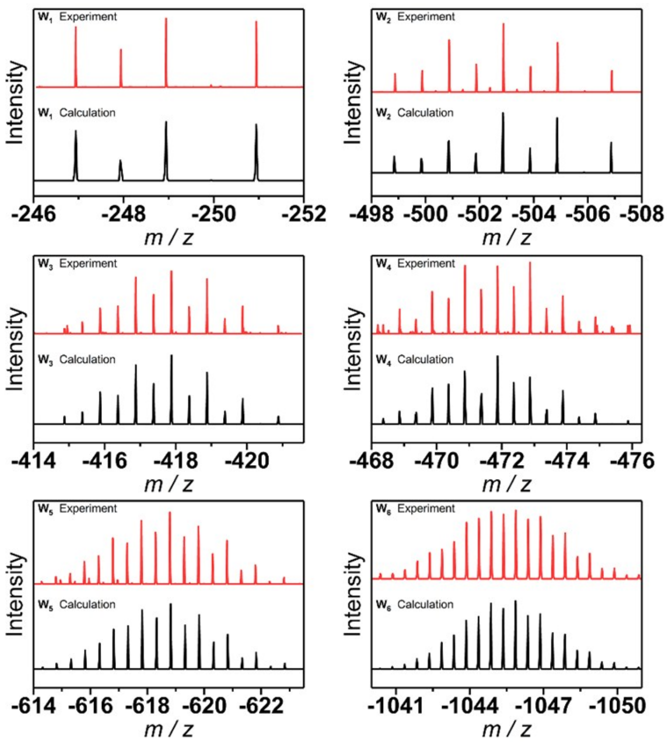


Fig. S10 Selected experimental (red) and simulated (black) mass spectra of the isotopic envelopes for **sol.W-HAc** in negative mode.

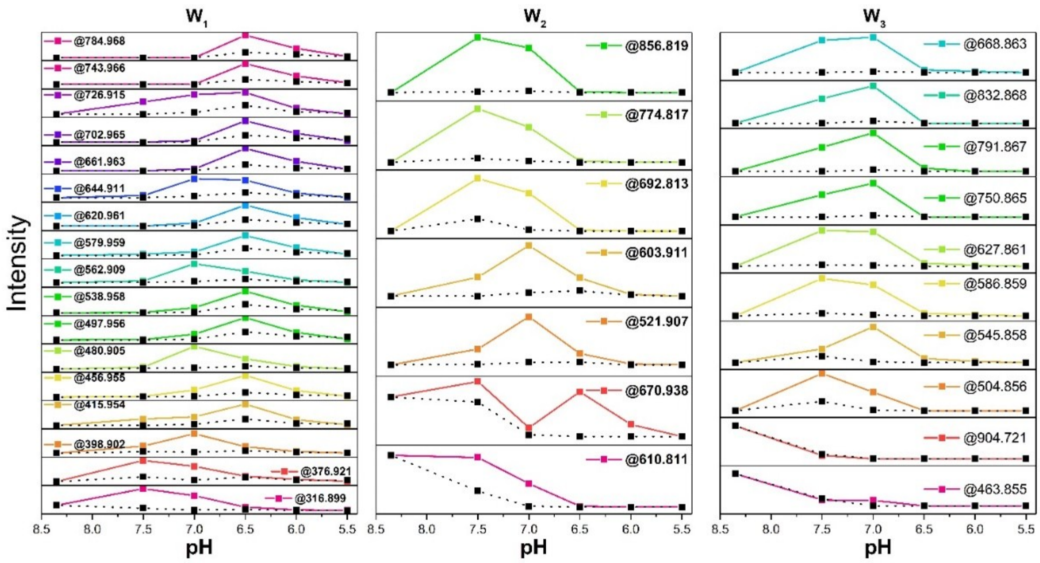


Fig. S11 Positive mode of ESI-MS spectral intensity-pH profiles of W_1, W_2 and W_3 species during the synthesis process in **sol.W-Mn**. The black dot lines represent corresponding intensities of the species in **sol.W-HAc.**

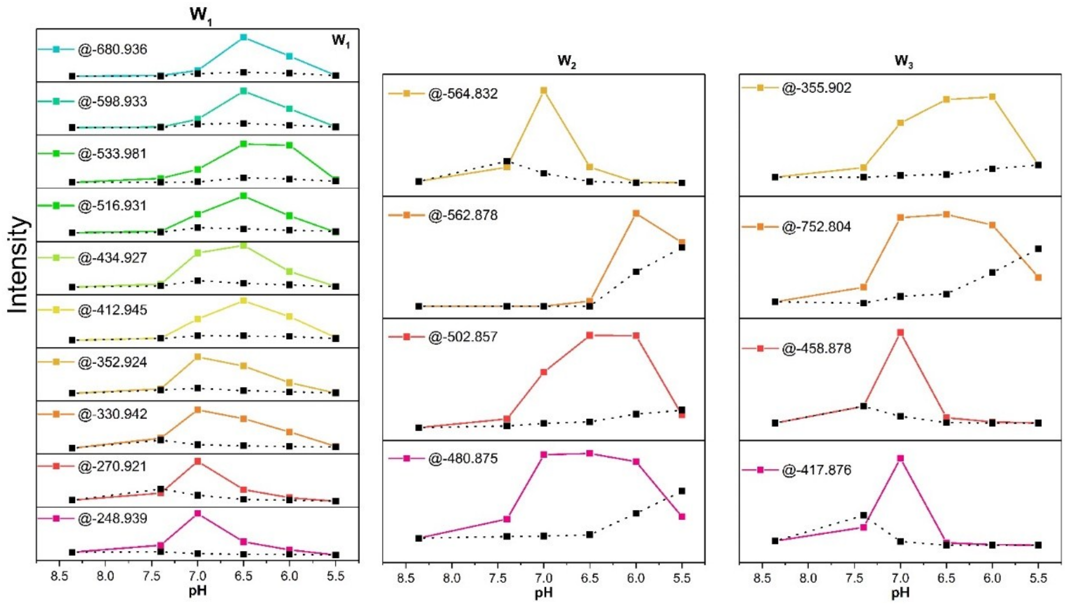


Fig. S12 Negative mode of ESI-MS spectral intensity-pH profiles of W_1, W_2 and W_3 species during the synthesis process in **sol.W-Mn**. The black dot lines represent corresponding intensities of the species in **sol.W-HAc**.

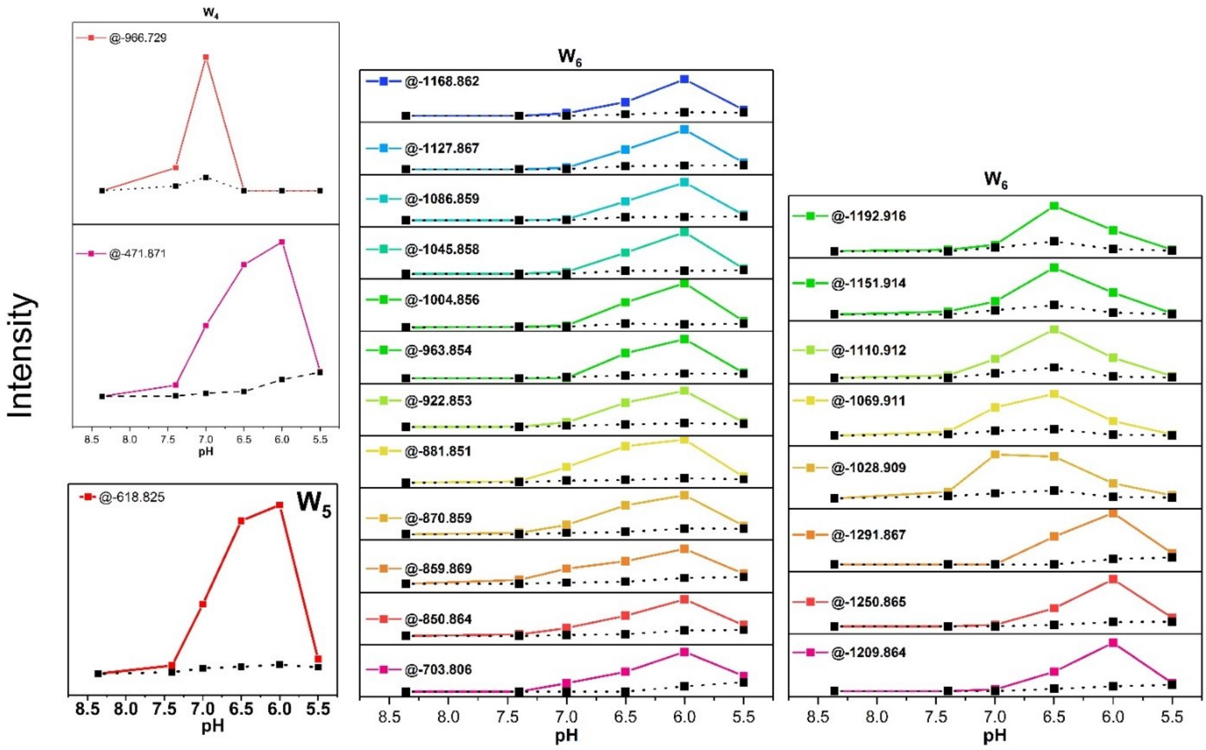


Fig. S13 Negative mode of ESI-MS spectral intensity-pH profiles of $\mathbf{W_4}$, $\mathbf{W_5}$ and $\mathbf{W_6}$ species during the synthesis process in **sol.W-Mn**. The black dot lines represent corresponding intensities of the species in **sol.W-HAc**.

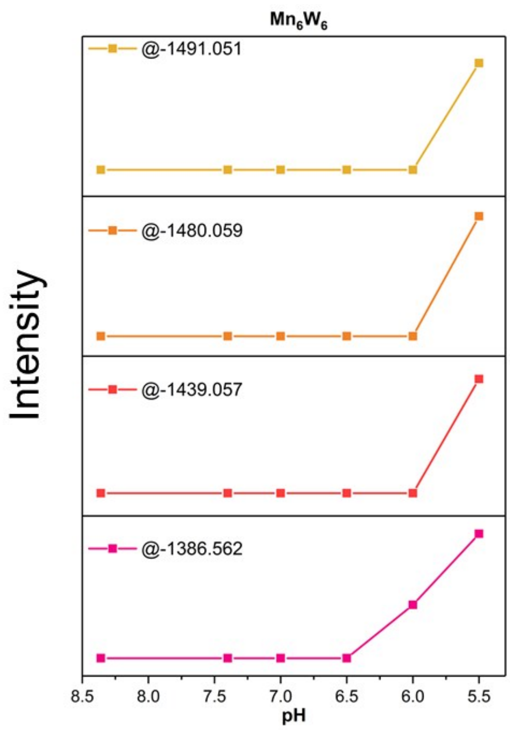


Fig. S14 Negative mode of ESI-MS spectral intensity-pH profiles of $\mathbf{Mn_6W_6}$ species during the synthesis process in **sol.W-Mn**.

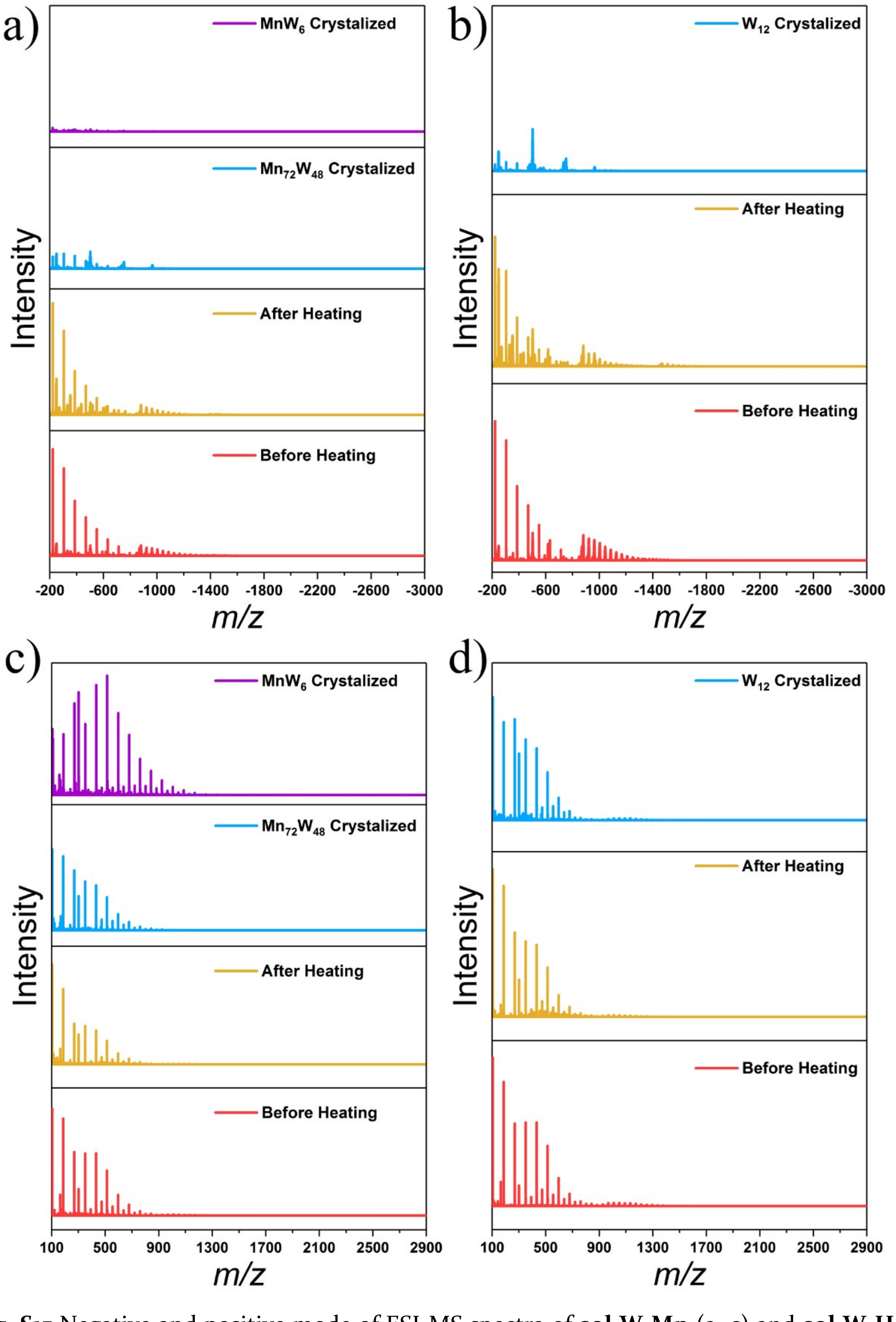


Fig. S15 Negative and positive mode of ESI-MS spectra of **sol.W-Mn** (a, c) and **sol.W-HAc** (b, d) in the course of crystallization.

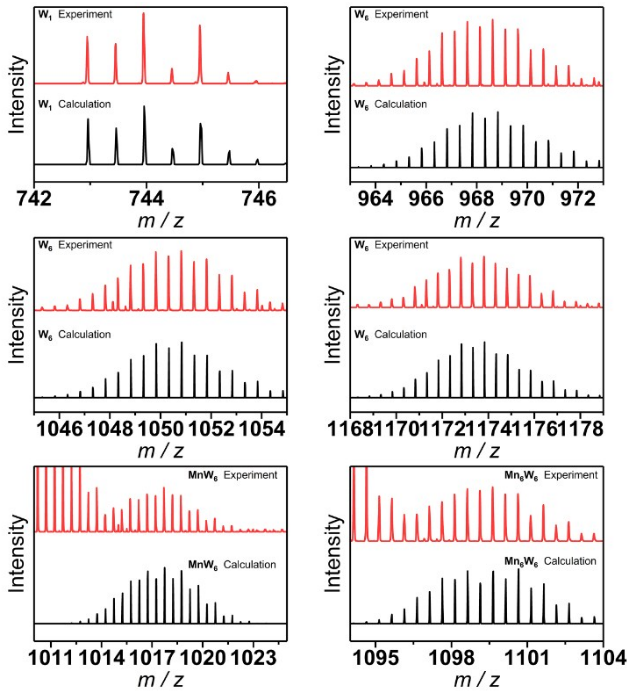


Fig. S16 Selected experimental (red) and simulated (black) positive mode mass spectra of the isotopic envelopes for **sol.W-Mn** in course of crystallization.

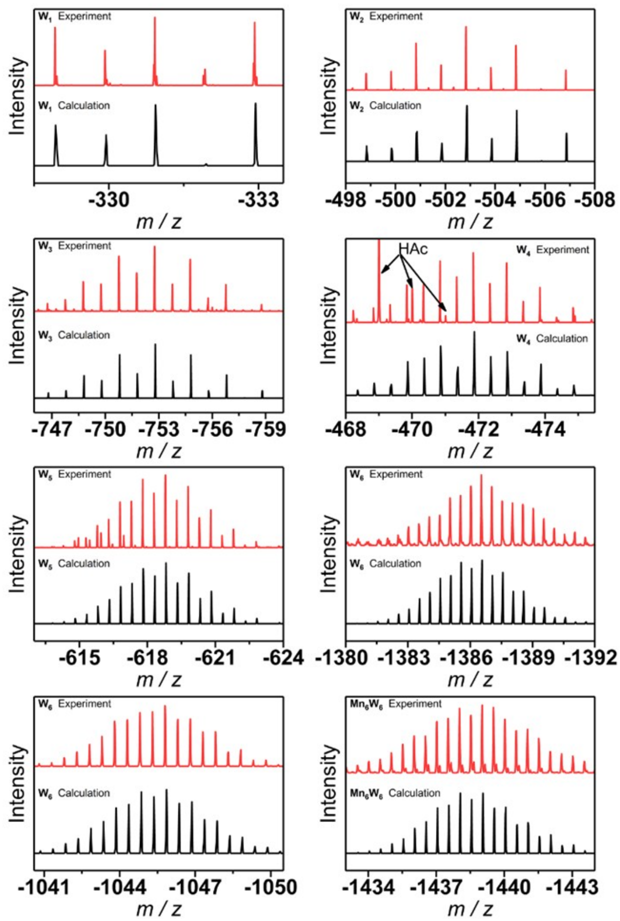


Fig. S17 Selected experimental (red) and simulated (black) negative mode mass spectra of the isotopic envelopes for **sol.W-Mn** in course of crystallization.

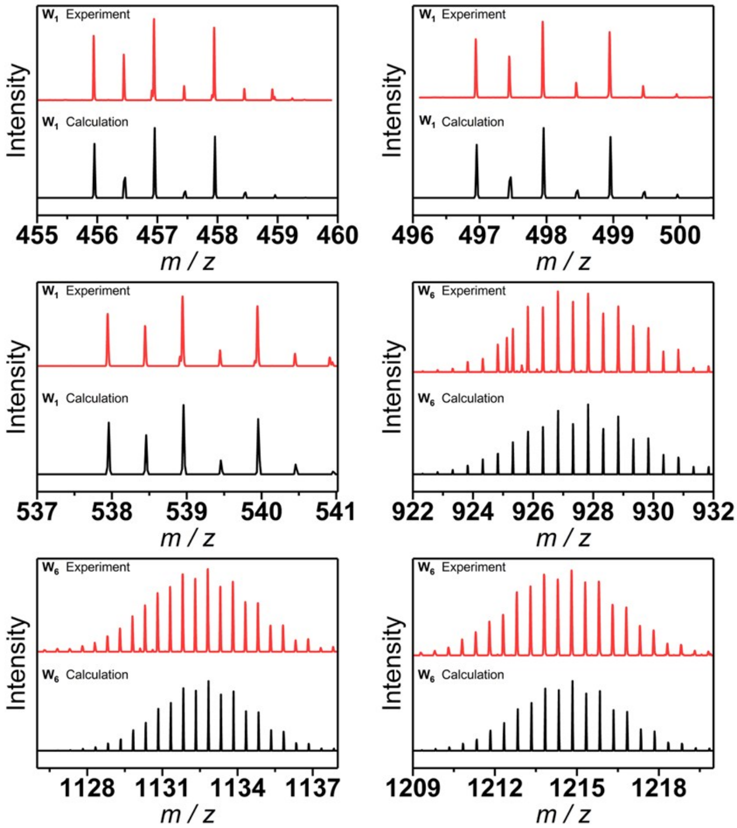


Fig. S18 Selected experimental (red) and simulated (black) positive mode mass spectra of the isotopic envelopes for **sol.W-HAc** in course of crystallization.

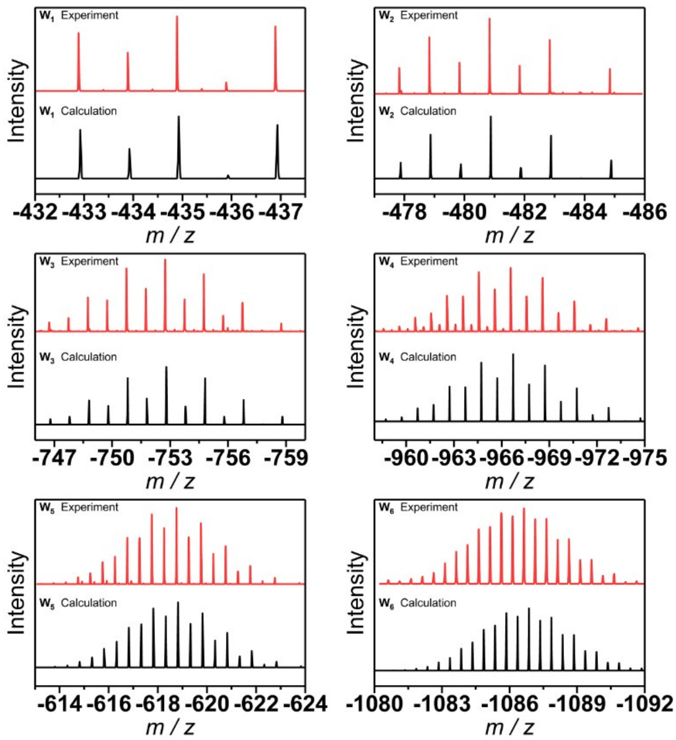


Fig. S19 Selected experimental (red) and simulated (black) negative mode mass spectra of the isotopic envelopes for **sol.W-HAc** in course of crystallization.

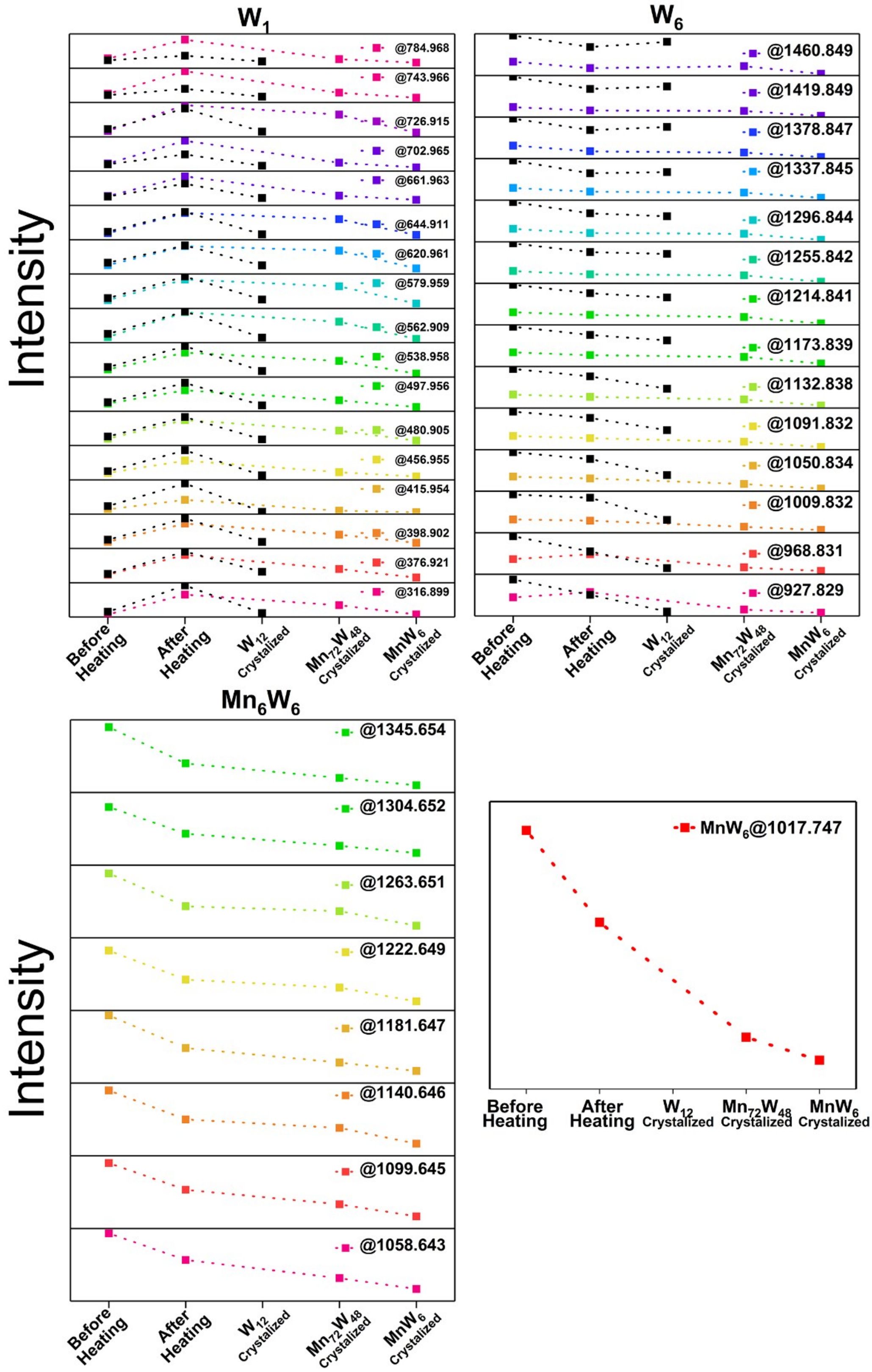


Fig. S20 Positive mode of ESI-MS spectral intensity-time profiles of $\mathbf{W_1}$, $\mathbf{W_6}$, $\mathbf{Mn_6W_6}$ and $\mathbf{MnW_6}$ species during the crystallization process in **sol.W-Mn**. The black dot lines represent corresponding intensities of the species in **sol.W-HAc** in course of crystallization.

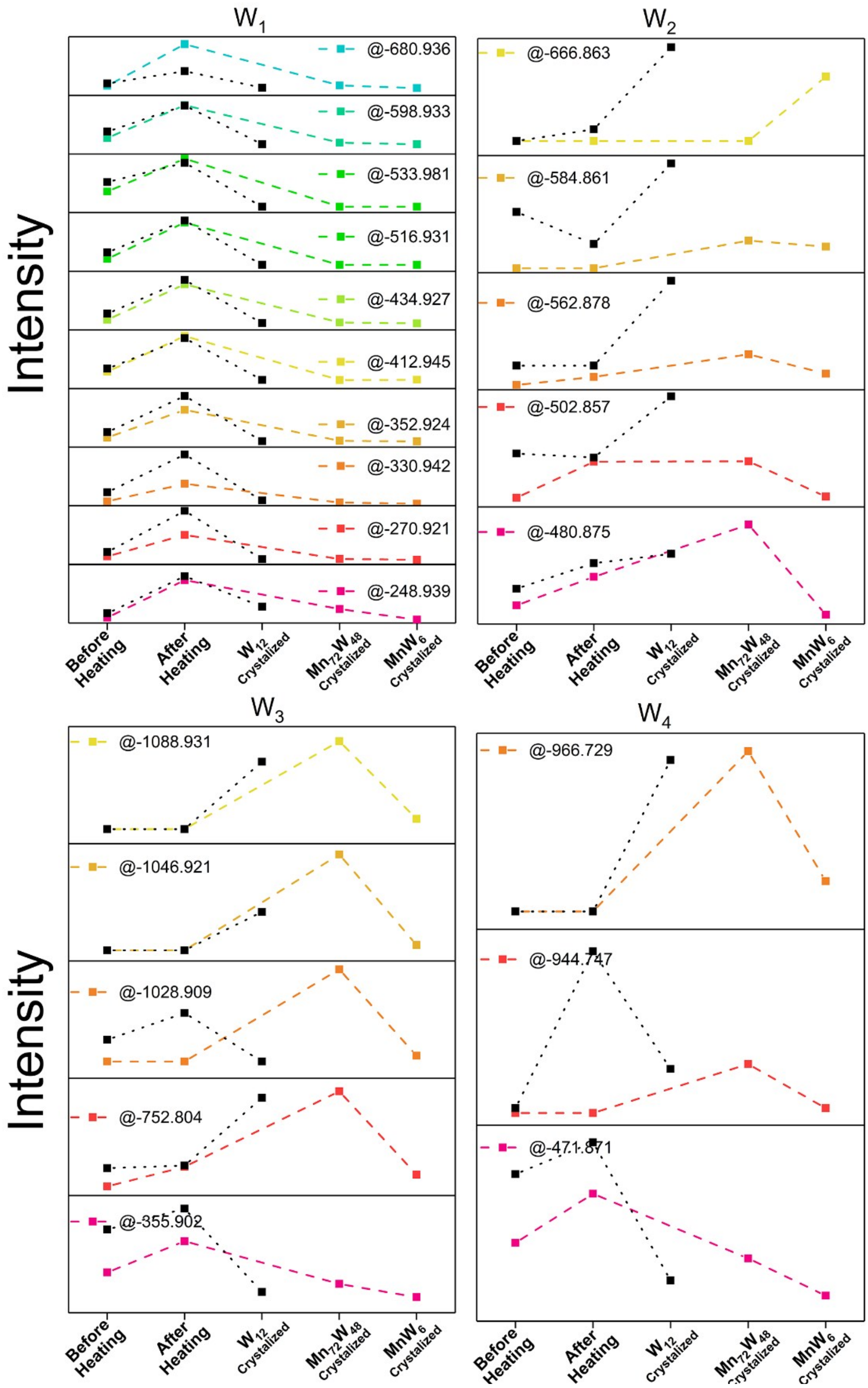


Fig. S21 Negative mode of ESI-MS spectral intensity-time profiles of $\mathbf{W_1}$, $\mathbf{W_2}$, $\mathbf{W_3}$ and $\mathbf{W_4}$ species during the crystallization process in **sol.W-Mn**. The black dot lines represent corresponding intensities of the species in **sol.W-HAc** in course of crystallization.

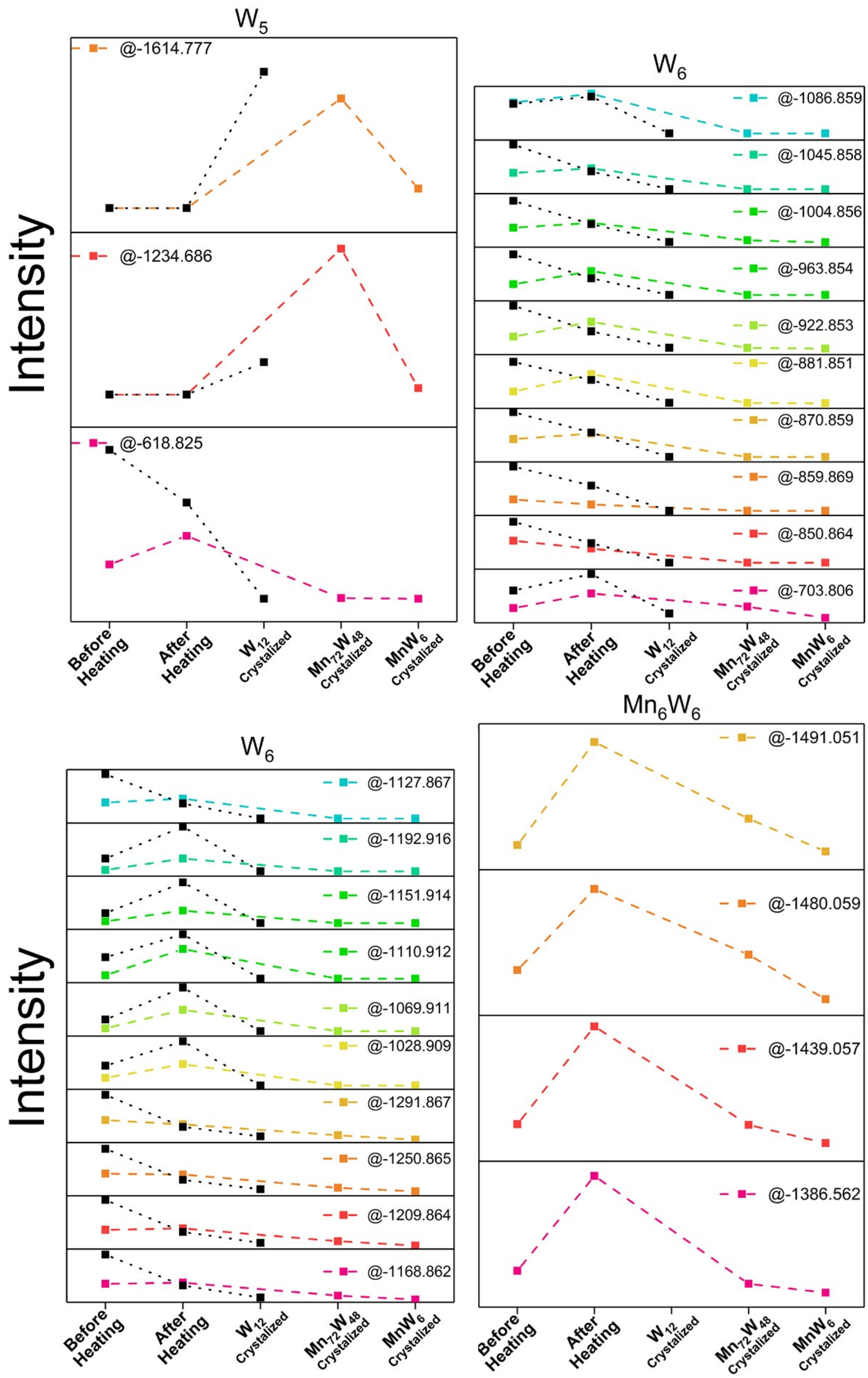


Fig. S22 Negative mode of ESI-MS spectral intensity-time profiles of $\mathbf{W_5}$, $\mathbf{W_6}$ and $\mathbf{Mn_6W_6}$ species during the crystallization process in **sol.W-Mn**. The black dot lines represent corresponding intensities of the species in **sol.W-HAc** in course of crystallization.

Table S2 Assignment of the key species identified in **sol.W-Mn** in positive mode of ESI-MS tests. (Both calculated and experimental m/z values refer to the most intense peak in the isotopic envelope)

Species	Entry	Identification	Cal. m/z	Exp. m/z
W_1	1	$Na_3WO_4^+$	316.899	316.905
	2	$Na_3WO_4(HAc)^+$	376.921	376.889
	3	$Na_3WO_4(NaAc)^+$	398.902	398.927
	4	$Na_4WO_4(NaAc)_6^{2+}$	415.954	415.987
	5	$Na_4WO_4(NaAc)_7^{2+}$	456.955	456.987
	6	$Na_3WO_4(NaAc)_2^+$	480.905	480.932
	7	$Na_4WO_4(NaAc)_8^{2+}$	497.956	497.981
	8	$Na_4WO_4(NaAc)_9^{2+}$	538.958	538.987
	9	$Na_3WO_4(NaAc)_3^+$	562.909	562.938
	10	$Na_4WO_4(NaAc)_{10}^{2+}$	579.959	579.967
	11	$Na_4WO_4(NaAc)_{11}^{2+}$	620.961	621.001
	12	$Na_3WO_4(NaAc)_4^+$	644.911	644.942
	13	$Na_4WO_4(NaAc)_{12}^{2+}$	661.963	661.999
	14	$Na_4WO_4(NaAc)_{13}^{2+}$	702.965	702.991
	15	$Na_3WO_4(NaAc)_5^+$	726.915	726.967
	16	$Na_4WO_4(NaAc)_{14}^{2+}$	743.966	743.997
	17	$Na_4WO_4(NaAc)_{15}^{2+}$	784.968	785.002
W_2	18	$Na_5W_2O_8^+$	610.811	610.823
	19	Na2H3W2O8(H2O)7$^+$	670.938	670.892
	20	Na6W2O8(NaAc)5^{2+}	521.907	521.956
	21	Na6W2O8(NaAc)7^{2+}	603.911	603.955
	22	Na5W2O8(NaAc)$^+$	692.813	692.852
	23	Na5W2O8(NaAc)2$^+$	774.817	774.849
	24	Na5W2O8(NaAc)3$^+$	856.819	856.853
W_3	25	$Na_8W_3O_{12}^{2+}$	463.855	463.864
	26	$Na_7W_3O_{12}^+$	904.721	904.741
	27	$Na_8W_3O_{12}(NaAc)^{2+}$	504.856	504.881
	28	$Na_8W_3O_{12}(NaAc)_2^{2+}$	545.858	545.879
	29	$Na_8W_3O_{12}(NaAc)_3^{2+}$	586.859	586.883
	30	$Na_8W_3O_{12}(NaAc)_4^{2+}$	627.861	627.889
	31	$Na_8W_3O_{12}(NaAc)_7^{2+}$	750.865	750.901
	32	$Na_8W_3O_{12}(NaAc)_8^{2+}$	791.867	791.897
	33	$Na_8W_3O_{12}(NaAc)_9^{2+}$	832.868	832.893

Species	Entry	Identification	Cal. m/z	Exp. m/z
	34	$Na_8W_3O_{12}(NaAc)_5^{2+}$	668.863	668.892
W_4	35	$Na_7H_3W_4O_{16}(H_2O)_7^{2+}$	640.874	640.835
W_5	36	$Na_{12}W_5O_{20}^{2+}$	757.765	757.782
	37	$Na_9H_3W_5O_{20}(H2O)_7^{2+}$	787.829	787.794
W_6	38	$Na_2H_2W_6O_{19}(NaAc)_4(H_2O)_4^{2+}$	927.829	927.838
	39	$Na_2H_2W_6O_{19}(NaAc)_5(H_2O)_4^{2+}$	968.831	968.844
	40	$Na_2H_2W_6O_{19}(NaAc)_6(H_2O)_4^{2+}$	1009.832	1009.855
	41	$Na_2H_2W_6O_{19}(NaAc)_7(H_2O)_4^{2+}$	1050.835	1050.858
	42	$Na_2H_2W_6O_{19}(NaAc)_8(H_2O)_4^{2+}$	1091.832	1091.867
	43	$Na_2H_2W_6O_{19}(NaAc)_9(H_2O)_4^{2+}$	1132.838	1132.865
	44	$Na_2H_2W_6O_{19}(NaAc)_{10}(H_2O)_4^{2+}$	1173.839	1173.871
	45	$Na_2H_2W_6O_{19}(NaAc)_{11}(H_2O)_4^{2+}$	1214.841	1214.869
	46	$Na_2H_2W_6O_{19}(NaAc)_{12}(H_2O)_4^{2+}$	1255.842	1255.863
	47	$Na_2H_2W_6O_{19}(NaAc)_{13}(H_2O)_4^{2+}$	1296.844	1296.877
	48	$Na_2H_2W_6O_{19}(NaAc)_{14}(H_2O)_4^{2+}$	1337.845	1337.874
	49	$Na_2H_2W_6O_{19}(NaAc)_{15}(H_2O)_4^{2+}$	1378.847	1378.873
	50	$Na_2H_2W_6O_{19}(NaAc)_{16}(H_2O)_4^{2+}$	1419.849	1419.879
	51	$Na_2H_2W_6O_{19}(NaAc)_{17}(H_2O)_4^{2+}$	1460.849	1460.881
	52	$Na_4W_6O_{19}(NaAc)_7(HAc)_4^{2+}$	1156.838	1156.826
	53	$Na_4W_6O_{19}(NaAc)_8(HAc)_4^{2+}$	1197.839	1197.831
	54	$Na_4W_6O_{19}(NaAc)_9(HAc)_4^{2+}$	1238.841	1238.849
	55	$Na_4W_6O_{19}(NaAc)_{10}(HAc)_4^{2+}$	1279.842	1279.851
	56	$Na_4W_6O_{19}(NaAc)_{11}(HAc)_4^{2+}$	1320.844	1320.855
MnW_6	57	$Na_8H_2MnW_6O_{23}(NaAc)_3(HAc)(OH)^{2+}$	1017.747	1017.723
Mn_6W_6	58	$NaH_{15}Mn_6W_6O_{37}(H_2O)_3^{2+}$	1058.643	1058.691
	59	$NaH_{15}Mn_6W_6O_{37}(H_2O)_3(NaAc)^{2+}$	1099.645	1099.688
	60	$NaH_{15}Mn_6W_6O_{37}(H_2O)_3(NaAc)_2^{2+}$	1140.646	1140.695
	61	$NaH_{15}Mn_6W_6O_{37}(H_2O)_3(NaAc)_3^{2+}$	1181.647	1181.701
	62	$NaH_{15}Mn_6W_6O_{37}(H_2O)_3(NaAc)_4^{2+}$	1222.649	1222.699
	63	$NaH_{15}Mn_6W_6O_{37}(H_2O)_3(NaAc)_5^{2+}$	1263.651	1263.679
	64	$NaH_{15}Mn_6W_6O_{37}(H_2O)_3(NaAc)_6^{2+}$	1304.652	1304.702
	65	$NaH_{15}Mn_6W_6O_{37}(H_2O)_3(NaAc)_7^{2+}$	1345.654	1345.697

Table S3 Assignment of the key species identified in **sol.W-Mn** in negative mode of ESI-MS tests. (Both calculated and experimental m/z values refer to the most intense peak in the isotopic envelope)

Species	Entry	Identification	Cal. m/z	Exp. m/z
W_1	1	HWO_4^-	-248.939	-248.935
	2	$NaWO_4^-$	-270.921	-270.933
	3	$HWO_4(NaAc)^-$	-330.942	-330.957
	4	$NaWO_4(NaAc)^-$	-352.924	-352.922
	5	$HWO_4(NaAc)_2^-$	-412.945	-412.958
	6	$NaWO_4(NaAc)_2^-$	-434.927	-434.927
	7	$NaWO_4(NaAc)_3^-$	-516.931	-516.932
	8	$WO_4(NaAc)_{10}^{2-}$	-533.981	-534.001
	9	$NaWO_4(NaAc)_4^-$	-598.933	-598.938
	10	$NaWO_4(NaAc)_5^-$	-680.936	-680.961
W_2	11	$HW_2O_7^-$	-480.875	-480.876
	12	$NaW_2O_7^-$	-502.857	-502.857
	13	$Na_3W_2O_8^-$	-564.832	-564.833
	14	$HW_2O_7(NaAc)^-$	-562.878	-562.901
W_3	15	$Na_4W_3O_{12}^{2-}$	-417.876	-417.876
	16	$W_3O_{10}^{2-}$	-355.902	-355.901
	17	$Na_4W_3O_{12}(NaAc)^{2-}$	-458.878	-458.879
	18	$NaW_3O_{10}(H_2O)^-$	-752.804	-752.798
W_4	19	$W_4O_{13}^{2-}$	-471.871	-471.869
	20	$NaW_4O_{13}^-$	-966.729	-966.735
W_5	21	$Na_2W_5O_{17}^{2-}$	-618.825	-618.827
W_6	22	$W_6O_{19}^{2-}$	-703.806	-703.811
	23	$W_6O_{19}(HAc)_4(H_2O)_3^{2-}$	-850.864	-850.849
	24	$W_6O_{19}(HAc)_4(H_2O)_4^{2-}$	-859.869	-859.857
	25	$W_6O_{19}(HAc)_2(NaAc)_4(H2O)_4^{2-}$	-870.859	-870.848
	26	$W_6O_{19}(HAc)_2(NaAc)_2(H_2O)_4^{2-}$	-881.851	-881.841
	27	$W_6O_{19}(HAc)_2(NaAc)_3(H_2O)_4^{2-}$	-922.853	-922.848
	28	$W_6O_{19}(HAc)_2(NaAc)_4(H_2O)_4^{2-}$	-963.854	-963.853

Species	Entry	Identification	Cal. m/z	Exp. m/z
	29	$W_6O_{19}(HAc)_2(NaAc)_5(H_2O)_4^{2-}$	-1004.856	-1004.862
	30	$W_6O_{19}(HAc)_2(NaAc)_6(H_2O)_4^{2-}$	-1045.858	-1045.869
	31	$W_6O_{19}(HAc)_2(NaAc)_7(H_2O)_4^{2-}$	-1086.859	-1086.859
	32	$W_6O_{19}(HAc)_2(NaAc)_8(H_2O)_4^{2-}$	-1127.867	-1127.869
	33	$W_6O_{19}(HAc)_2(NaAc)_9(H_2O)_4^{2-}$	-1168.862	-1168.873
	34	$W_6O_{19}(HAc)_2(NaAc)_{10}(H_2O)_4^{2-}$	-1209.864	-1209.872
	35	$W_6O_{19}(HAc)_2(NaAc)_{11}(H_2O)_4^{2-}$	-1250.865	-1250.876
	36	$W_6O_{19}(HAc)_2(NaAc)_{12}(H_2O)_4^{2-}$	-1291.867	-1291.871
	37	$W_6O_{19}(HAc)_6(NaAc)_2(H_2O)_7^{2-}$	-1028.909	-1028.838
	38	$W_6O_{19}(HAc)_6(NaAc)_3(H_2O)_7^{2-}$	-1069.911	-1069.841
	39	$W_6O_{19}(HAc)_6(NaAc)_4(H_2O)_7^{2-}$	-1110.912	-1110.851
	40	$W_6O_{19}(HAc)_6(NaAc)_5(H_2O)_7^{2-}$	-1151.914	-1151.862
	41	$W_6O_{19}(HAc)_6(NaAc)_6(H_2O)_7^{2-}$	-1192.916	-1192.856
Mn_6W_6	46	$Na_{12}Mn_6W_6O_{37}(NaAc)_4(H_2O)_8^{2-}$	-1386.562	-1386.634
	47	$Na_{13}Mn_6W_6O_{37}(NaAc)_5(H_2O)_8^{2-}$	-1439.057	-1439.106
	48	$Na_{13}Mn_6W_6O_{37}(NaAc)_6(H_2O)_8^{2-}$	-1480.059	-1480.099
	49	$Na_{14}Mn_6W_6O_{37}(OH)(NaAc)_6(H_2O)_7^{2-}$	-1491.051	-1491.088

Table S4 Assignment of the key species identified in **sol.W-HAc** in positive mode of ESI-MS tests. (Both calculated and experimental m/z values refer to the most intense peak in the isotopic envelope)

Species	Entry	Identification	Cal. m/z	Exp. m/z
W_1	1	$Na_3WO_4^+$	316.899	316.903
	2	$Na_3WO_4(HAc)^+$	376.921	376.901
	3	$Na_3WO_4(NaAc)^+$	398.902	398.911
	4	$Na_4WO_4(NaAc)_6^{2+}$	415.954	415.976
	5	$Na_4WO_4(NaAc)_7^{2+}$	456.955	456.982
	6	$Na_3WO_4(NaAc)_2^+$	480.905	480.929
	7	$Na_4WO_4(NaAc)_8^{2+}$	497.956	497.979
	8	$Na_4WO_4(NaAc)_9^{2+}$	538.958	538.976
	9	$Na_3WO_4(NaAc)_3^+$	562.909	562.933

Species	Entry	Identification	Cal. m/z	Exp. m/z
	10	$Na_4WO_4(NaAc)_{10}^{2+}$	579.959	579.971
	11	$Na_4WO_4(NaAc)_{11}^{2+}$	620.961	620.973
	12	$Na_3WO_4(NaAc)_4^{+}$	644.911	644.943
	13	$Na_4WO_4(NaAc)_{12}^{2+}$	661.963	661.978
	14	$Na_4WO_4(NaAc)_{13}^{2+}$	702.965	702.987
	15	$Na_3WO_4(NaAc)_5^{+}$	726.915	726.923
	16	$Na_4WO_4(NaAc)_{14}^{2+}$	743.966	743.977
	17	$Na_4WO_4(NaAc)_{15}^{2+}$	784.968	784.988
W_2	18	$Na_5W_2O_8^{+}$	610.811	610.827
	19	$Na_2H_3W_2O_8(H_2O)_7^{+}$	670.938	670.898
	20	$Na_6W_2O_8(NaAc)_5^{2+}$	521.907	521.945
	21	$Na_6W_2O_8(NaAc)_7^{2+}$	603.911	603.952
	22	$Na_5W_2O_8(NaAc)^{+}$	692.813	692.847
	23	$Na_5W_2O_8(NaAc)_2^{+}$	774.817	774.801
	24	$Na_5W_2O_8(NaAc)_3^{+}$	856.819	856.778
W_3	25	$Na_8W_3O_{12}^{2+}$	463.855	463.849
	26	$Na_7W_3O_{12}^{+}$	904.721	904.702
	27	$Na_8W_3O_{12}(NaAc)^{2+}$	504.856	504.865
	28	$Na_8W_3O_{12}(NaAc)_2^{2+}$	545.858	545.842
	29	$Na_8W_3O_{12}(NaAc)_3^{2+}$	586.859	586.837
	30	$Na_8W_3O_{12}(NaAc)_4^{2+}$	627.861	627.847
	31	$Na_8W_3O_{12}(NaAc)_7^{2+}$	750.865	750.889
	32	$Na_8W_3O_{12}(NaAc)_8^{2+}$	791.867	791.876
	33	$Na_8W_3O_{12}(NaAc)_9^{2+}$	832.868	832.883
	34	$Na_8W_3O_{12}(NaAc)_5^{2+}$	668.863	668.854
W_4	35	$Na_7H_3W_4O_{16}(H_2O)_7^{2+}$	640.874	640.856
W_5	36	$Na_{12}W_5O_{20}^{2+}$	757.765	757.786
	37	$Na_9H_3W_5O_{20}(H_2O)_7^{2+}$	787.829	787.801
W_6	38	$Na_2H_2W_6O_{19}(NaAc)_4(H_2O)_4^{2+}$	927.829	927.836
	39	$Na_2H_2W_6O_{19}(NaAc)_5(H_2O)_4^{2+}$	968.831	968.841
	40	$Na_2H_2W_6O_{19}(NaAc)_6(H_2O)_4^{2+}$	1009.832	1009.853
	41	$Na_2H_2W_6O_{19}(NaAc)_7(H_2O)_4^{2+}$	1050.835	1050.856
	42	$Na_2H_2W_6O_{19}(NaAc)_8(H_2O)_4^{2+}$	1091.832	1091.863
	43	$Na_2H_2W_6O_{19}(NaAc)_9(H_2O)_4^{2+}$	1132.838	1132.859

Species	Entry	Identification	Cal. m/z	Exp. m/z
	44	$Na_2H_2W_6O_{19}(NaAc)_{10}(H_2O)_4^{2+}$	1173.839	1173.862
	45	$Na_2H_2W_6O_{19}(NaAc)_{11}(H_2O)_4^{2+}$	1214.841	1214.871
	46	$Na_2H_2W_6O_{19}(NaAc)_{12}(H_2O)_4^{2+}$	1255.842	1255.869
	47	$Na_2H_2W_6O_{19}(NaAc)_{13}(H_2O)_4^{2+}$	1296.844	1296.871
	48	$Na_2H_2W_6O_{19}(NaAc)_{14}(H_2O)_4^{2+}$	1337.845	1337.872
	49	$Na_2H_2W_6O_{19}(NaAc)_{15}(H_2O)_4^{2+}$	1378.847	1378.869
	50	$Na_2H_2W_6O_{19}(NaAc)_{16}(H_2O)_4^{2+}$	1419.849	1419.873
	51	$Na_2H_2W_6O_{19}(NaAc)_{17}(H_2O)_4^{2+}$	1460.849	1460.778
	52	$Na_4W_6O_{19}(NaAc)_7(HAc)_4^{2+}$	1156.838	1156.826
	53	$Na_4W_6O_{19}(NaAc)_8(HAc)_4^{2+}$	1197.839	1197.831
	54	$Na_4W_6O_{19}(NaAc)_9(HAc)_4^{2+}$	1238.841	1238.849
	55	$Na_4W_6O_{19}(NaAc)_{10}(HAc)_4^{2+}$	1279.842	1279.851
	56	$Na_4W_6O_{19}(NaAc)_{11}(HAc)_4^{2+}$	1320.844	1320.855

Table S5 Assignment of the key species identified in **sol.W-HAc** in negative mode of ESI-MS tests. (Both calculated and experimental m/z values refer to the most intense peak in the isotopic envelope)

Species	Entry	Identification	Cal. m/z	Exp. m/z
W_1	1	HWO_4^-	-248.939	-248.941
	2	$NaWO_4^-$	-270.921	-270.923
	3	$HWO_4(NaAc)^-$	-330.942	-330.924
	4	$NaWO_4(NaAc)^-$	-352.924	-352.929
	5	$HWO_4(NaAc)_2^-$	-412.945	-412.953
	6	$NaWO_4(NaAc)_2^-$	-434.927	-434.937
	7	$NaWO_4(NaAc)_3^-$	-516.931	-516.943
	8	$WO_4(NaAc)_{10}^{2-}$	-533.981	534.001
	9	$NaWO_4(NaAc)_4^-$	-598.933	-598.966
	10	$NaWO_4(NaAc)_5^-$	-680.936	-680.973
W_2	11	$HW_2O_7^-$	-480.875	-480.887
	12	$NaW_2O_7^-$	-502.857	-502.871
	13	$Na_3W_2O_8^-$	-564.832	-564.847
	14	$HW_2O_7(NaAc)^-$	-562.878	-562.881
W_3	15	$Na_4W_3O_{12}^{2-}$	-417.876	-417.885

Species	Entry	Identification	Cal. m/z	Exp. m/z
	16	$W_3O_{10}^{2-}$	-355.902	-355.899
	17	$Na_4W_3O_{12}(NaAc)^{2-}$	-458.878	-458.889
	18	$NaW_3O_{10}(H_2O)^{-}$	-752.804	-752.843
W_4	19	$W_4O_{13}^{2-}$	-471.871	-471.896
	20	$NaW_4O_{13}^{-}$	-966.729	-966.768
W5	21	$Na_2W_5O_{17}^{2-}$	-618.825	-618.838
W_6	22	$W_6O_{19}^{2-}$	-703.806	-703.822
	23	$W_6O_{19}(HAc)_4(H_2O)_3^{2-}$	-850.864	-850.882
	24	$W_6O_{19}(HAc)_4(H2O)_4^{2-}$	-859.869	-859.845
	25	$W_6O_{19}(HAc)_2(NaAc)_4(H_2O)_4^{2-}$	-870.859	-870.838
	26	$W_6O_{19}(HAc)_2(NaAc)_2(H_2O)_4^{2-}$	-881.851	-881.874
	27	$W_6O_{19}(HAc)_2(NaAc)_3(H_2O)_4^{2-}$	-922.853	-922.883
	28	$W_6O_{19}(HAc)_2(NaAc)_4(H_2O)_4^{2-}$	-963.854	-963.841
	29	$W_6O_{19}(HAc)_2(NaAc)_5(H_2O)_4^{2-}$	-1004.856	-1004.845
	30	$W_6O_{19}(HAc)_2(NaAc)_6(H_2O)_4^{2-}$	-1045.858	-1045.851
	31	$W_6O_{19}(HAc)_2(NaAc)_7(H_2O)_4^{2-}$	-1086.859	-1086.857
	32	$W_6O_{19}(HAc)_2(NaAc)_8(H_2O)_4^{2-}$	-1127.867	-1127.864
	33	$W_6O_{19}(HAc)_2(NaAc)_9(H_2O)_4^{2-}$	-1168.862	-1168.869
	34	$W_6O_{19}(HAc)_2(NaAc)_{10}(H_2O)_4^{2-}$	-1209.864	-1209.871
	35	$W_6O_{19}(HAc)_2(NaAc)_{11}(H_2O)_4^{2-}$	-1250.865	-1250.879
	36	$W_6O_{19}(HAc)_2(NaAc)_{12}(H_2O)_4^{2-}$	-1291.867	-1291.873
	37	$W_6O_{19}(HAc)_6(NaAc)_2(H_2O)_7^{2-}$	-1028.909	-1028.891
	38	$W_6O_{19}(HAc)_6(NaAc)_3(H_2O)_7^{2-}$	-1069.911	-1069.887
	39	$W_6O_{19}(HAc)_6(NaAc)_4(H_2O)_7^{2-}$	-1110.912	-1110.885
	40	$W_6O_{19}(HAc)_6(NaAc)_5(H_2O)_7^{2-}$	-1151.914	-1151.889
	41	$W_6O_{19}(HAc)_6(NaAc)_6(H_2O)_7^{2-}$	-1192.916	-1192.877

Table S6 Assignment of the key species identified in **sol.W-Mn** for crystallization course in positive mode of ESI-MS tests. (Both calculated and experimental m/z values refer to the most intense peak in the isotopic envelope)

Species	Entry	Identification	Cal. m/z	Exp. m/z

W_1	1	$Na_3WO_4^+$	316.899	316.866
	2	$Na_3WO_4(HAc)^+$	376.921	376.881
	3	$Na_3WO_4(NaAc)^+$	398.902	398.856
	4	$Na_4WO_4(NaAc)_6^{2+}$	415.954	415.911
	5	$Na_4WO_4(NaAc)_7^{2+}$	456.955	456.908
	6	$Na_3WO_4(NaAc)_2^+$	480.905	480.867
	7	$Na_4WO_4(NaAc)_8^{2+}$	497.956	497.905
	8	$Na_4WO_4(NaAc)_9^{2+}$	538.958	538.903
	9	$Na_3WO_4(NaAc)_3^+$	562.909	562.879
	10	$Na_4WO_4(NaAc)_{10}^{2+}$	579.959	579.921
	11	$Na_4WO_4(NaAc)_{11}^{2+}$	620.961	620.936
	12	$Na_3WO_4(NaAc)_4^+$	644.911	644.896
	13	$Na_4WO_4(NaAc)_{12}^{2+}$	661.963	661.932
	14	$Na_4WO_4(NaAc)_{13}^{2+}$	702.965	702.966
	15	$Na_3WO_4(NaAc)_5^+$	726.915	726.912
	16	$Na_4WO_4(NaAc)_{14}^{2+}$	743.966	743.963
	17	$Na_4WO_4(NaAc)_{15}^{2+}$	784.968	784.954
W_6	18	$Na_2H_2W_6O_{19}(NaAc)_4(H_2O)_4^{2+}$	927.829	927.756
	19	$Na_2H_2W_6O_{19}(NaAc)_5(H_2O)_4^{2+}$	968.831	968.762
	20	$Na_2H_2W_6O_{19}(NaAc)_6(H_2O)_4^{2+}$	1009.832	1009.763
	21	$Na_2H_2W_6O_{19}(NaAc)_7(H_2O)_4^{2+}$	1050.834	1050.753
	22	$Na_2H_2W_6O_{19}(NaAc)_8(H_2O)_4^{2+}$	1091.832	1091.758
	23	$Na_2H_2W_6O_{19}(NaAc)_9(H_2O)_4^{2+}$	1132.838	1132.761
	24	$Na_2H_2W_6O_{19}(NaAc)_{10}(H_2O)_4^{2+}$	1173.839	1173.763
	25	$Na_2H_2W_6O_{19}(NaAc)_{11}(H_2O)_4^{2+}$	1214.841	1214.767
	26	$Na_2H_2W_6O_{19}(NaAc)_{12}(H_2O)_4^{2+}$	1255.842	1255.766
	27	$Na_2H_2W_6O_{19}(NaAc)_{13}(H_2O)_4^{2+}$	1296.844	1296.771
	28	$Na_2H_2W_6O_{19}(NaAc)_{14}(H_2O)_4^{2+}$	1337.845	1337.769
	29	$Na_2H_2W_6O_{19}(NaAc)_{15}(H2O)_4^{2+}$	1378.847	1378.778
	30	$Na_2H_2W_6O_{19}(NaAc)_{16}(H2O)_4^{2+}$	1419.849	1419.801
	31	$Na_2H_2W_6O_{19}(NaAc)_{17}(H2O)_4^{2+}$	1460.849	1460.811
MnW_6	32	$Na8H2MnW6O_{23}(NaAc)_3(HAc)(OH)^{2+}$	1017.747	1017.704
Mn_6W_6	34	$NaH_{15}Mn_6W_6O_{37}(H_2O)_3^{2+}$	1058.643	1058.708
	35	$NaH_{15}Mn_6W_6O_{37}(H_2O)_3(NaAc)^{2+}$	1099.645	1099.708
	36	$NaH_{15}Mn_6W_6O_{37}(H_2O)_3(NaAc)_2^{2+}$	1140.646	1140.706
	37	$NaH_{15}Mn_6W_6O_{37}(H_2O)_3(NaAc)_3^{2+}$	1181.647	1181.708
	38	$NaH_{15}Mn_6W_6O_{37}(H_2O)_3(NaAc)_4^{2+}$	1222.649	1222.708
	39	$NaH_{15}Mn_6W_6O_{37}(H_2O)_3(NaAc)_5^{2+}$	1263.651	1263.707
	40	$NaH_{15}Mn_6W_6O_{37}(H_2O)_3(NaAc)_6^{2+}$	1304.652	1304.706
	41	$NaH_{15}Mn_6W_6O_{37}(H_2O)_3(NaAc)_7^{2+}$	1345.654	1345.704

Table S7 Assignment of the key species identified in **sol.W-Mn** for crystallization course in negative mode of ESI-MS tests. (Both calculated and experimental m/z values refer to the most intense peak in the isotopic envelope)

Species	Entry	Identification	Cal. m/z	Exp. m/z
W_1	1	HWO_4^-	-248.939	-248.935
	2	$NaWO_4^-$	-270.921	-270.903
	3	$HWO_4(NaAc)^-$	-330.942	-330.922
	4	$NaWO_4(NaAc)^-$	-352.924	-352.916
	5	$HWO_4(NaAc)_2^-$	-412.945	-412.921
	6	$NaWO_4(NaAc)_2^-$	-434.927	-434.907
	7	$NaWO_4(NaAc)_3^-$	-516.931	-516.912
	8	$WO_4(NaAc)_{10}^{2-}$	-533.981	-533.956
	9	$NaWO_4(NaAc)_4^-$	-598.933	-598.907
	10	$NaWO_4(NaAc)_5^-$	-680.936	-680.901
W_2	11	$HW_2O_7^-$	-480.875	-480.881
	12	$NaW_2O_7^-$	-502.857	-502.858
	13	$HW_2O_7(NaAc)^-$	-562.878	-562.887
	14	$NaW_2O_7(NaAc)^-$	-584.861	-584.869
	15	$NaW_2O_7(NaAc)_2^-$	-666.863	-666.875
W_3	16	$W_3O_{10}^{2-}$	-355.902	-355.881
	17	$NaW_3O_{10}(H_2O)^-$	-752.804	-752.807
	18	$NaW_3O_{10}(HAc)_4(H_2O)_3^-$	-1028.909	-1028.836
	19	$NaW_3O_{10}(HAc)_4(H_2O)_4^-$	-1046.921	-1046.843
	20	$NaW_3O_{10}(HAc)_5(H_2O)_3^-$	-1088.931	-1088.871
W_4	21	$W_4O_{13}^{2-}$	-471.871	-471.889
	22	$HW_4O_{13}^-$	-944.747	-944.651
	23	$NaW_4O_{13}^-$	-966.729	-966.737
W_5	24	$Na_2W_5O_{17}^{2-}$	-618.825	-618.793
	25	$NaW_5O_{16}(H_2O)_2^-$	-1234.686	-1234.709
	26	$NaW_5O_{16}(NaAc)_2(HAc)_3(H_2O)_4^-$	-1614.777	-1614.723
W_6	27	$W_6O_{19}^{2-}$	-703.806	-703.771
	28	$W_6O_{19}(HAc)_4(H_2O)_3^{2-}$	-850.864	-850.783
	29	$W_6O_{19}(HAc)_4(H_2O)_4^{2-}$	-859.869	-859.789
	30	$W_6O_{19}(HAc)_3(NaAc)(H_2O)_4^{2-}$	-870.859	-870.792
	31	$W_6O_{19}(HAc)_2(NaAc)_2(H_2O)_4^{2-}$	-881.851	-881.776

Species	Entry	Identification	Cal. m/z	Exp. m/z
	32	$W_6O_{19}(HAc)_2(NaAc)_3(H_2O)_4^{2-}$	-922.853	-922.787
	33	$W_6O_{19}(HAc)_2(NaAc)_4(H_2O)_4^{2-}$	-963.854	-963.798
	34	$W_6O_{19}(NaAc)_5(H_2O)_4(HAc)_2^{2-}$	-1004.856	-1004.796
	35	$W_6O_{19}(NaAc)_6(H_2O)_4(HAc)_2^{2-}$	-1045.858	-1045.801
	36	$W_6O_{19}(NaAc)_7(H_2O)_4(HAc)_2^{2-}$	-1086.859	-1086.803
	37	$W_6O_{19}(NaAc)_8(H_2O)_4(HAc)_2^{2-}$	-1127.867	-1127.823
	38	$W_6O_{19}(NaAc)_9(H_2O)_4(HAc)_2^{2-}$	-1168.862	-1168.819
	39	$W_6O_{19}(NaAc)_{10}(H_2O)_4(HAc)_2^{2-}$	-1209.864	-1209.831
	40	$W_6O_{19}(NaAc)_{11}(H_2O)_4(HAc)_2^{2-}$	-1250.865	-1250.837
	41	$W_6O_{19}(NaAc)_{12}(H_2O)_4(HAc)_2^{2-}$	-1291.867	-1291.843
	42	$W_6O_{19}(HAc)_6(NaAc)_2(H_2O)_7^{2-}$	-1028.909	-1028.841
	43	$W_6O_{19}(HAc)_6(NaAc)_3(H_2O)_7^{2-}$	-1069.911	-1069.851
	44	$W_6O_{19}(HAc)_6(NaAc)_4(H_2O)_7^{2-}$	-1110.912	-1110.856
	45	$W_6O_{19}(HAc)_6(NaAc)_5(H2O)_7^{2-}$	-1151.914	-1151.861
	46	$W_6O_{19}(HAc)_6(NaAc)_6(H2O)_7^{2-}$	-1192.916	-1192.867
Mn_6W_6	47	$Na_{12}Mn_6W_6O37(NaAc)_4(H_2O)_8^{2-}$	-1386.562	-1386.535
	48	$Na_{13}Mn_6W_6O_{37}(NaAc)_5(H_2O)_8^{2-}$	-1439.057	-1439.027
	49	$Na_{13}Mn_6W_6O_{37}(NaAc)_6(H_2O)_8^{2-}$	-1480.059	-1480.023
	50	$Na_{14}Mn_6W_6O_{37}(OH)(NaAc)_6(H_2O)_7^{2-}$	-1491.051	-1491.017

Table S8 Assignment of the key species identified in **sol.W-HAc** for crystallization course in positive mode of ESI-MS tests. (Both calculated and experimental m/z values refer to the most intense peak in the isotopic envelope)

Species	Entry	Identification	Cal. m/z	Exp. m/z
W_1	1	$Na_3WO_4^+$	316.899	316.891
	2	$Na_3WO_4(HAc)^+$	376.921	376.912
	3	$Na_3WO_4(NaAc)^+$	398.902	398.893
	4	$Na_4WO_4(NaAc)_6^{2+}$	415.954	415.943
	5	$Na_4WO_4(NaAc)_7^{2+}$	456.955	456.943
	6	$Na_3WO_4(NaAc)_2^+$	480.905	480.892
	7	$Na_4WO_4(NaAc)_8^{2+}$	497.956	497.943
	8	$Na_4WO_4(NaAc)_9^{2+}$	538.958	538.944
	9	$Na_3WO_4(NaAc)_3^+$	562.909	562.894
	10	$Na_4WO_4(NaAc)_{10}^{2+}$	579.959	579.944
	11	$Na_4WO_4(NaAc)_{11}^{2+}$	620.961	620.946

Species	Entry	Identification	Cal. m/z	Exp. m/z
	12	$Na_3WO_4(NaAc)_4^+$	644.911	644.892
	13	$Na_4WO_4(NaAc)_{12}^{2+}$	661.963	661.946
	14	$Na_4WO_4(NaAc)_{13}^{2+}$	702.965	702.948
	15	$Na_3WO_4(NaAc)_5^+$	726.915	726.897
	16	$Na_4WO_4(NaAc)_{14}^{2+}$	743.966	743.951
	17	$Na_4WO_4(NaAc)_{15}^{2+}$	784.968	784.948
W_6	18	$Na_2H_2W_6O_{19}(NaAc)_4(H_2O)_4^{2+}$	927.829	927.766
	19	$Na_2H_2W_6O_{19}(NaAc)_5(H_2O)_4^{2+}$	968.831	968.771
	20	$Na_2H_2W_6O_{19}(NaAc)_6(H_2O)_4^{2+}$	1009.832	1009.771
	21	$Na_2H_2W_6O_{19}(NaAc)_7(H_2O)_4^{2+}$	1050.834	1050.769
	22	$Na_2H_2W_6O_{19}(NaAc)_8(H2O)_4^{2+}$	1091.832	1091.764
	23	$Na_2H_2W_6O_{19}(NaAc)_9(H2O)_4^{2+}$	1132.838	1132.768
	24	$Na_2H_2W_6O_{19}(NaAc)_{10}(H_2O)_4^{2+}$	1173.839	1173.763
	25	$Na_2H_2W_6O_{19}(NaAc)_{11}(H_2O)_4^{2+}$	1214.841	1214.785
	26	$Na_2H_2W_6O_{19}(NaAc)_{12}(H_2O)_4^{2+}$	1255.842	1255.778
	27	$Na_2H_2W_6O_{19}(NaAc)_{13}(H_2O)_4^{2+}$	1296.844	1296.779
	28	$Na_2H_2W_6O_{19}(NaAc)_{14}(H_2O)_4^{2+}$	1337.845	1337.775
	29	$Na_2H_2W_6O_{19}(NaAc)_{15}(H_2O)_4^{2+}$	1378.847	1378.796
	30	$Na_2H_2W_6O_{19}(NaAc)_{16}(H_2O)_4^{2+}$	1419.849	1419.811
	31	$Na_2H_2W_6O_{19}(NaAc)_{17}(H_2O)_4^{2+}$	1460.849	1460.814

Table S9 Assignment of the key species identified in **sol.W-HAc** for crystallization course in negative mode of ESI-MS tests. (Both calculated and experimental m/z values refer to the most intense peak in the isotopic envelope)

Species	Entry	Identification	Cal. m/z	Exp. m/z
W_1	1	HWO_4^-	-248.939	-248.911
	2	$NaWO_4^-$	-270.921	-270.893
	3	$HWO_4(NaAc)^-$	-330.942	-330.926
	4	$NaWO_4(NaAc)^-$	-352.924	-352.913
	5	$HWO_4(NaAc)_2^-$	-412.945	-412.916
	6	$NaWO_4(NaAc)_2^-$	-434.927	-434.911
	7	$NaWO_4(NaAc)_3^-$	-516.931	-516.901
	8	$WO_4(NaAc)_{10}^{2-}$	-533.981	-533.953
	9	$NaWO_4(NaAc)_5^-$	-680.936	-680.967
	10	$NaWO_4(NaAc)_4^-$	-598.933	-598.911
W_2	11	$HW_2O_7^-$	-480.875	-480.869
	12	$NaW_2O_7^-$	-502.857	-502.806

Species	Entry	Identification	Cal. m/z	Exp. m/z
	13	$HW_2O_7(NaAc)^-$	-562.878	-562.862
	14	$NaW_2O_7(NaAc)^-$	-584.861	-584.857
	15	$NaW_2O_7(NaAc)_2^-$	-666.863	-666.851
W_3	16	$W_3O_{10}^{2-}$	-355.902	-355.872
	17	$NaW_3O_{10}(H_2O)^-$	-752.804	-752.792
	18	$NaW_3O_{10}(HAc)_4(H_2O)_3^-$	-1028.909	-1028.836
	19	$NaW_3O_{10}(HAc)_4(H_2O)_4^-$	-1046.921	-1046.843
	20	$NaW_3O_{10}(HAc)_5(H_2O)_3^-$	-1088.931	-1088.871
W_4	21	$W_4O_{13}^{2-}$	-471.871	-471.843
	22	$HW_4O_{13}^-$	-944.747	-944.678
	23	$NaW_4O_{13}^-$	-966.729	-966.699
W_5	24	$Na_2W_5O_{17}^{2-}$	-618.825	-618.783
	25	$NaW_5O_{16}(H_2O)_2^-$	-1234.686	-1234.701
	26	$NaW_5O_{16}(NaAc)_2(HAc)_3(H_2O)_4^-$	-1614.777	-1614.701
W_6	27	$W_6O_{19}^{2-}$	-703.806	-703.773
	28	$W_6O_{19}(HAc)_4(H_2O)_3^{2-}$	-850.864	-850.820
	29	$W_6O_{19}(HAc)_4(H_2O)_4^{2-}$	-859.869	-859.811
	30	$W_6O_{19}(HAc)_3(NaAc)(H_2O)_4^{2-}$	-870.859	-870.801
	31	$W_6O_{19}(HAc)_2(NaAc)_2(H_2O)_4^{2-}$	-881.851	-881.807
	32	$W_6O_{19}(HAc)_2(NaAc)_3(H_2O)_4^{2-}$	-922.853	-922.814
	33	$W_6O_{19}(HAc)_2(NaAc)_4(H_2O)_4^{2-}$	-963.854	-963.908
	34	$W_6O_{19}(NaAc)_5(H_2O)_4(HAc)_2^{2-}$	-1004.856	-1004.801
	35	$W_6O_{19}(NaAc)_6(H_2O)_4(HAc)_2^{2-}$	-1045.858	-1045.808
	36	$W_6O_{19}(NaAc)_7(H_2O)_4(HAc)_2^{2-}$	-1086.859	-1086.802
	37	$W_6O_{19}(NaAc)_8(H_2O)_4(HAc)_2^{2-}$	-1127.867	-1127.821
	38	$W_6O_{19}(NaAc)_9(H_2O)_4(HAc)_2^{2-}$	-1168.862	-1168.811
	39	$W_6O_{19}(NaAc)_{10}(H_2O)_4(HAc)_2^{2-}$	-1209.864	-1209.837
	40	$W_6O_{19}(NaAc)_{11}(H_2O)_4(HAc)_2^{2-}$	-1250.865	-1250.834
	41	$W_6O_{19}(NaAc)_{12}(H_2O)_4(HAc)_2^{2-}$	-1291.867	-1291.843
	42	$W_6O_{19}(HAc)_6(NaAc)_2(H2O)_7^{2-}$	-1028.909	-1028.889
	43	$W_6O_{19}(HAc)_6(NaAc)_3(H_2O)_7^{2-}$	-1069.911	-1069.877
	44	$W_6O_{19}(HAc)_6(NaAc)_4(H_2O)_7^{2-}$	-1110.912	-1110.845
	45	$W_6O_{19}(HAc)_6(NaAc)_5(H_2O)_7^{2-}$	-1151.914	-1151.874
	46	$W_6O_{19}(HAc)_6(NaAc)_6(H_2O)_7^{2-}$	-1192.916	-1192.865