

Supporting Information

Synthesis and Mechanism Studies of a High-Nuclear Mn₇₂W₄₈ Cluster

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Experimental section

The failure synthesis methods of Mn₇₂W₄₈

Method S1. Na₂MoO₄ + sol.Mn: 3 g Na₂MoO₄·2H₂O (12.43 mmol) was dissolved in 30 mL H₂O (0.1 g/mL), and the pH of the solution was adjusted to about 5.5-5.8 with **sol.Mn**. Then, the mixture was heated to 90 °C for 1 h, cooled to room temperature and filtered. The resulting golden orange filtrate was left to evaporate at room temperature, and only Waugh type crystal Na₆MnMo₉O₃₂·zH₂O was obtained after 1-2 weeks.

Method S2. MnW₆ as precursor: MnW₆ (collected as by-products from **sol.W-Mn**, 1.5 g) and 2 g Na₂WO₄·2H₂O (6.01 mmol) were dissolved in 30 mL H₂O. The pH of the mixed solution was adjusted to 5.5 with a 60% HAc solution. Subsequently, the resulting brown mixture was heated to 90 °C for 1 h, cooled to room temperature, and filtered. The resulting orange color filtrate was left to evaporate at room temperature, but only paratungstate **W₁₂** could be obtained before the mother liquid dried up.

Method S3. W₁₂ + sol.Mn: Paratungstate **W₁₂** crystals (3 g, contains 11.58 mmol W) were dissolved in 30 mL H₂O (0.1 g/mL), and the pH of the **W₁₂** solution was adjusted to 5.5 by **sol.Mn**. Then, the mixture was heated to 90 °C for 1 h and allowed to cool down at room temperature. The resulting reddish-brown filtrate was slowly evaporated at room temperature, and no crystals were obtained at the end.

Method S4. W₁₂ + solid Mn₁₂: Paratungstate **W₁₂** crystals (3 g, contains 11.58 mmol W) and solid **Mn₁₂** (0.3 g, contains 1.75 mmol Mn) were dissolved in 30 mL H₂O, and the pH of the mixed solution was adjusted to 5.5 by 1M NaAc solution. Subsequently, the reddish-brown mixture was heated to 90 °C for 1 h, cooled to room temperature, and filtered. The filtrate was slowly evaporated at room temperature, no crystals were obtained at the end.

Method S5. NaOH + sol.Mn + Na₂WO₄: 1 g NaOH (25 mmol) and 1.5 mL **sol.Mn** (0.85 mmol Mn) were dissolved in 30 mL H₂O, then 2 g Na₂WO₄·2H₂O (6.01 mmol) was added into the above solution with vigorous stirring. The pH of the mixed solution was adjusted to 5.5-6.0 by 60% HAc, and then the mixture was heated to 90 °C for 1 hour. After this period, the mixture was cooled to room temperature and filtered. The resulting yellow filtrate was evaporated at room temperature, only paratungstate **W₁₂** was obtained before the mother liquid dried up.

Results and Discussion

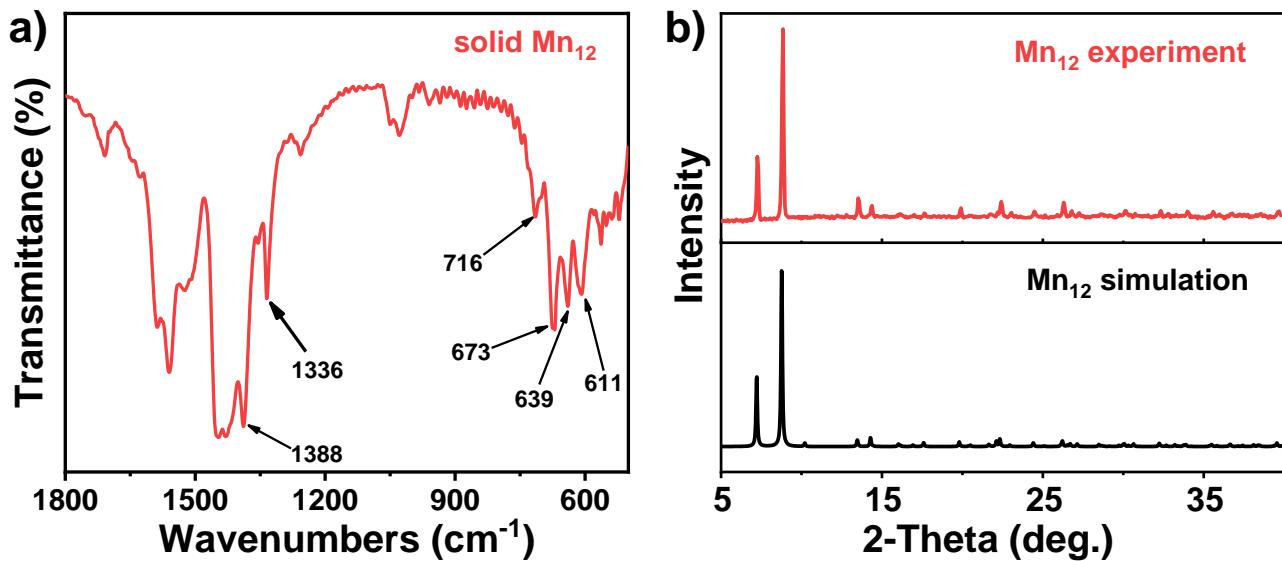


Figure S1. a) IR spectrum of Mn_{12} solid. b) XRD patterns of experiment and simulated Mn_{12} .

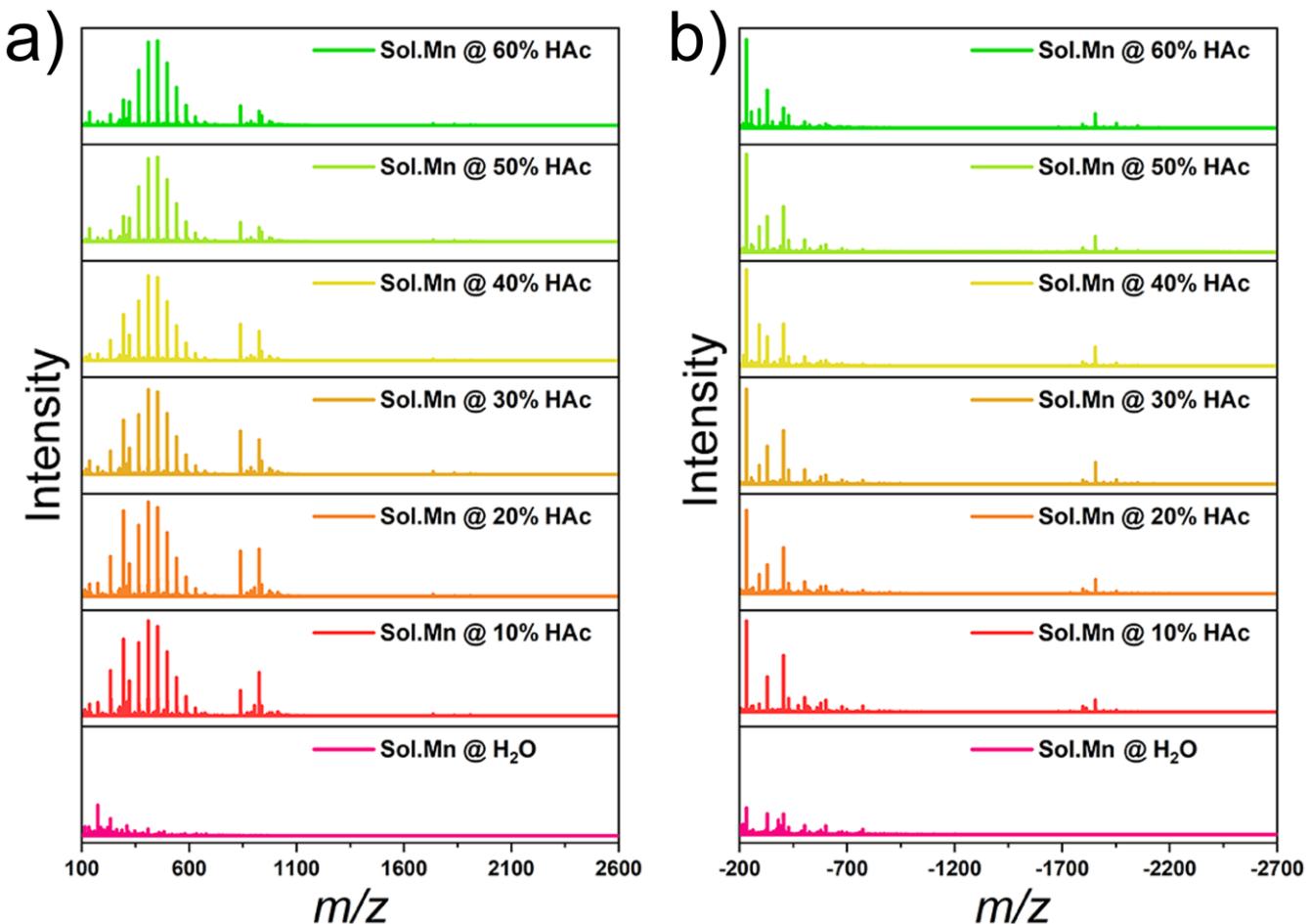


Figure S2. Positive (a) and negative (b) mode of ESI-MS full-scan spectra of sol.Mn in HAc solutions with different concentrations.

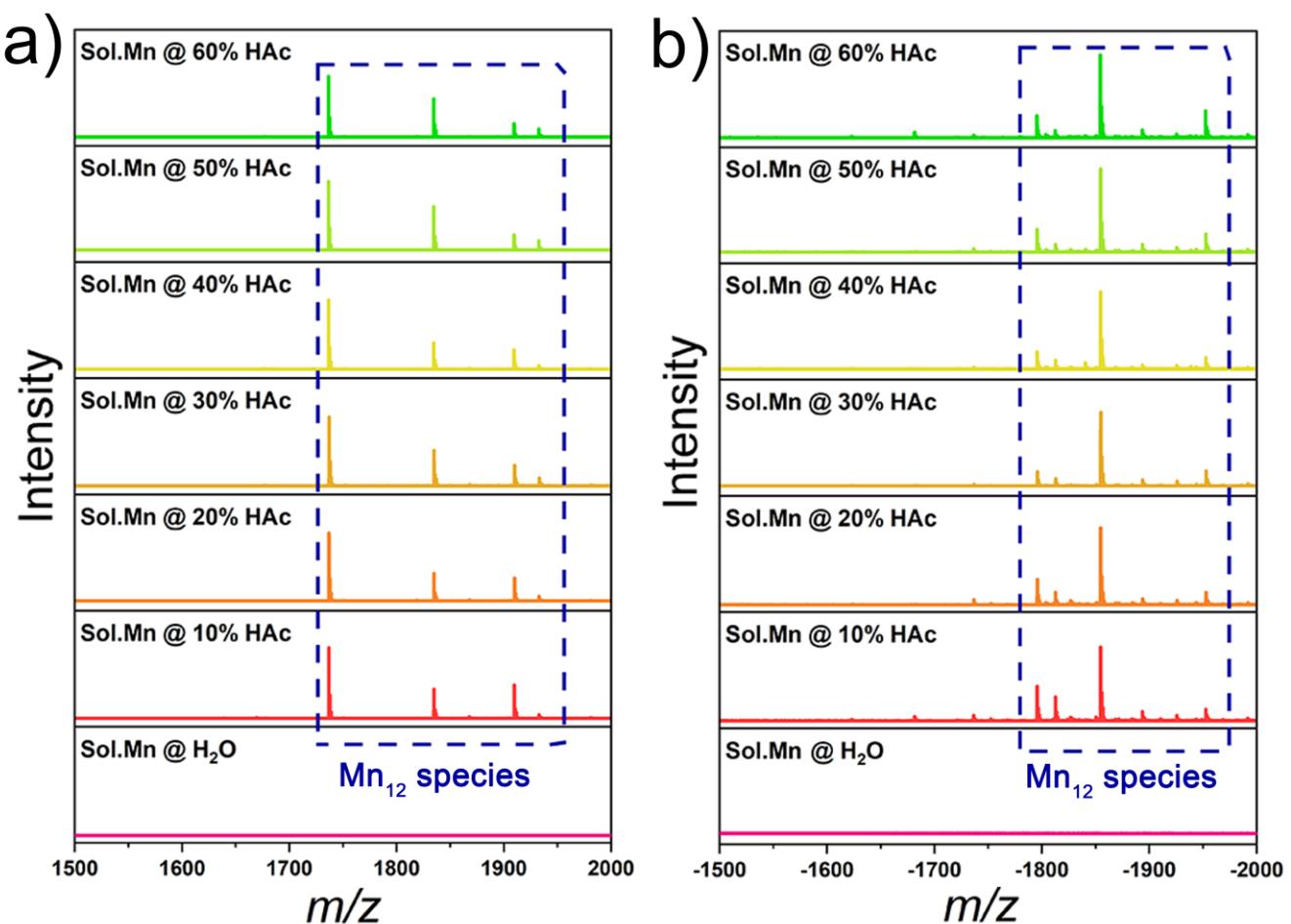


Figure S3. Positive (a) and negative (b) mode of ESI-MS spectra (scan ranges 1500-2000) of **sol.Mn** in HAc solutions with different concentration.

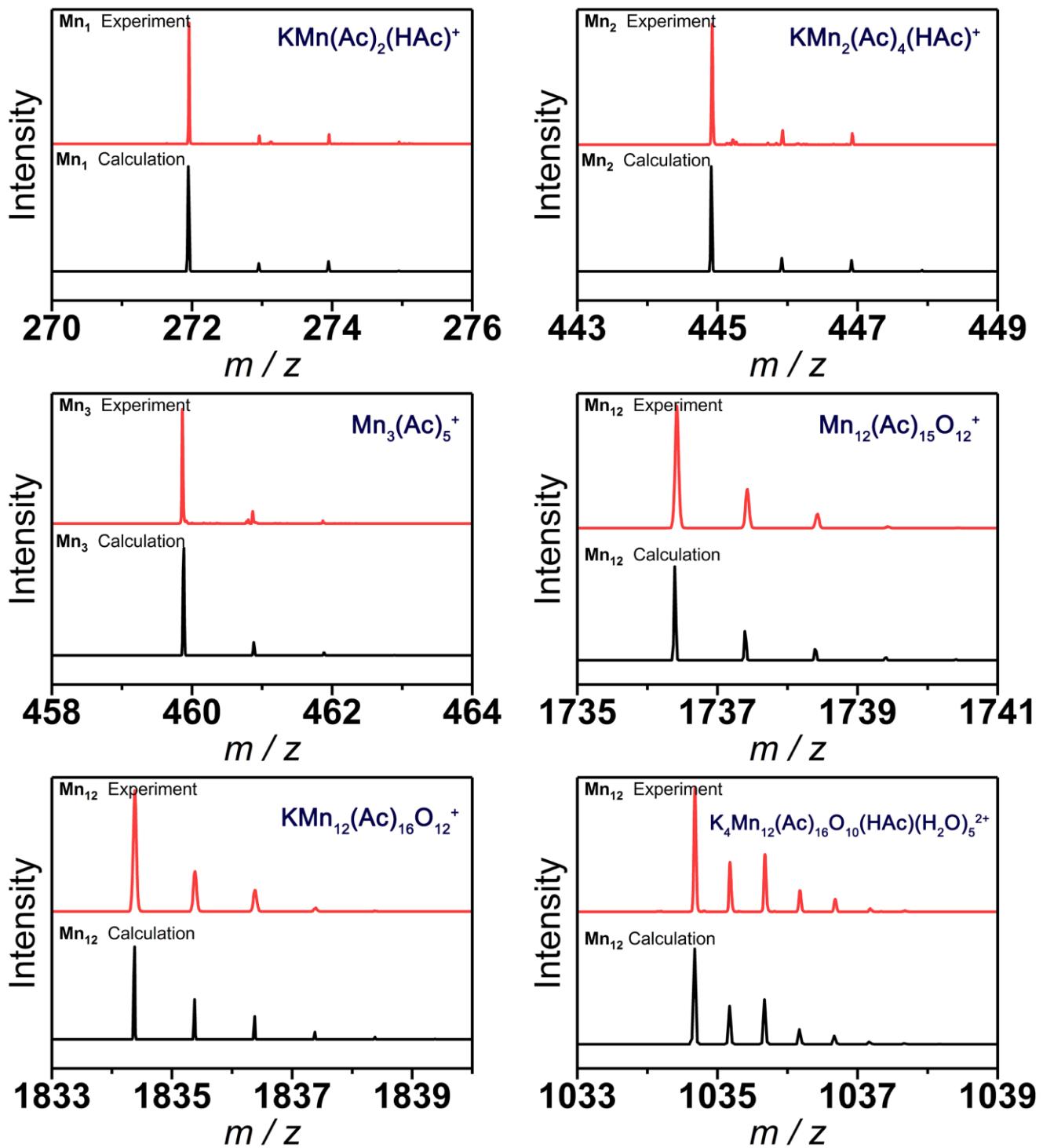


Figure S4. Selected experimental (red) and simulated (black) mass spectra of the isotopic envelopes for **sol.Mn** in positive mode.

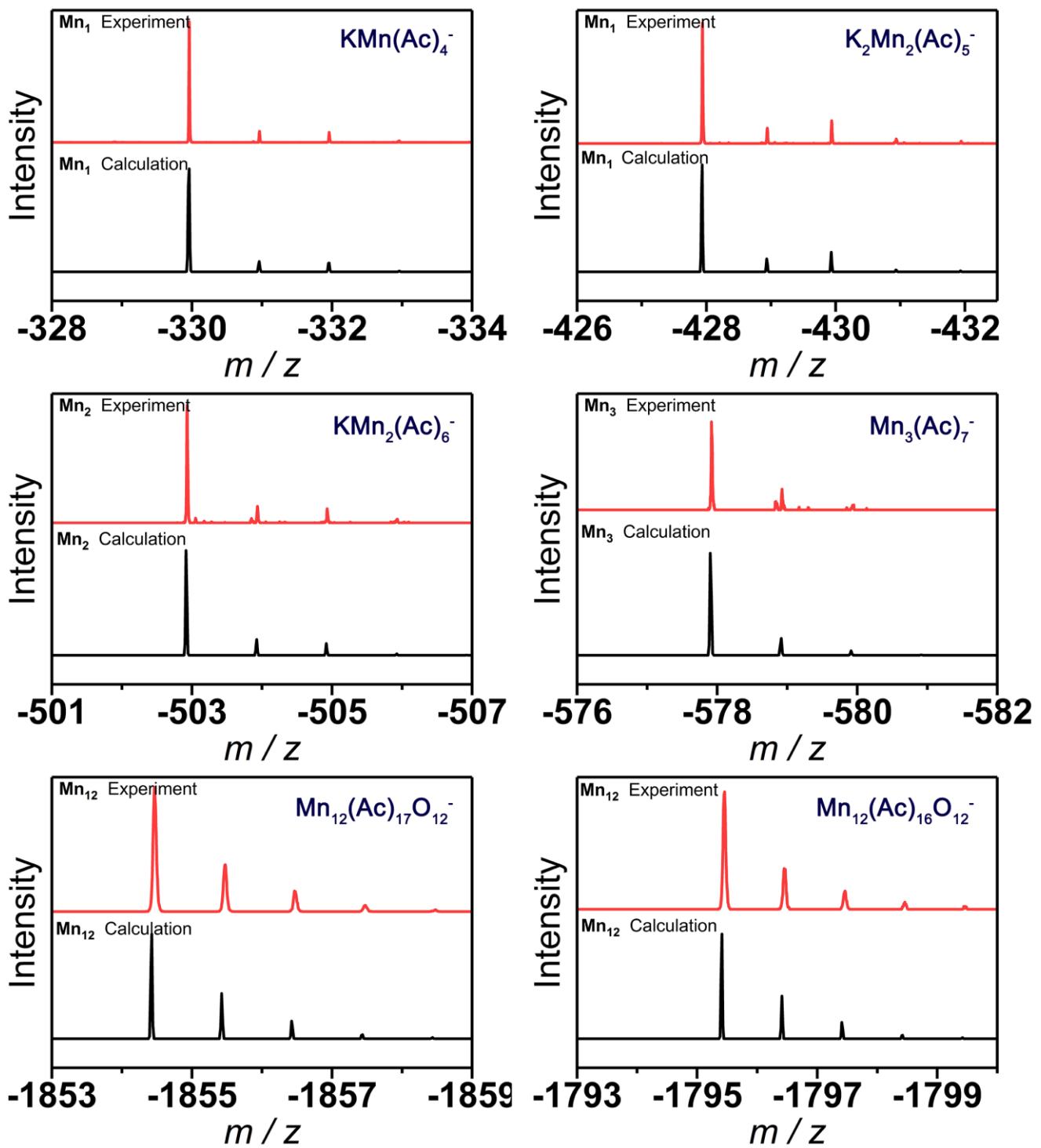


Figure S5. Selected experimental (red) and simulated (black) mass spectra of the isotopic envelopes for **sol.Mn** in negative mode.

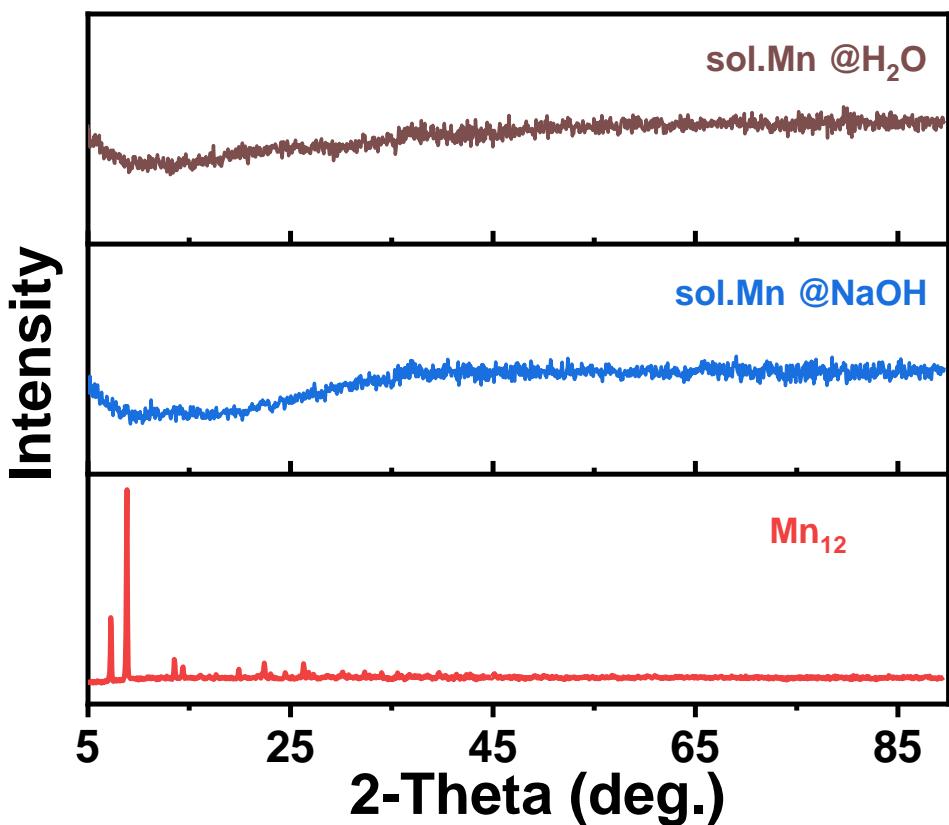


Figure S6. XRD patterns of **Mn₁₂** (red) and the solids of **sol.Mn** in NaOH (blue) and H₂O solution (brown) obtained by filtration.

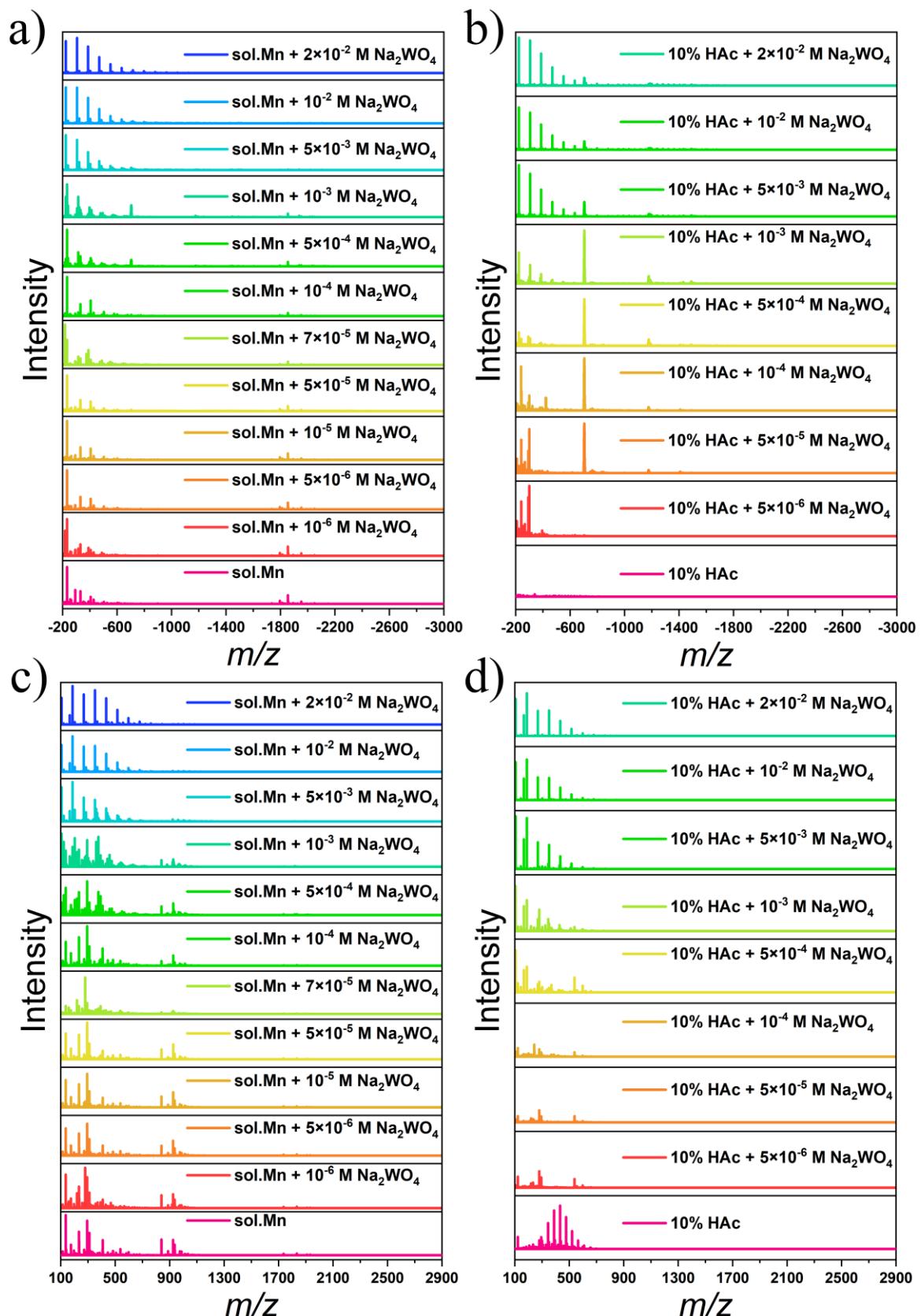


Figure S7. Negative and positive mode of ESI-MS spectra of a, c) **sol.Mn-W** and b, d).**sol.HAc-W**

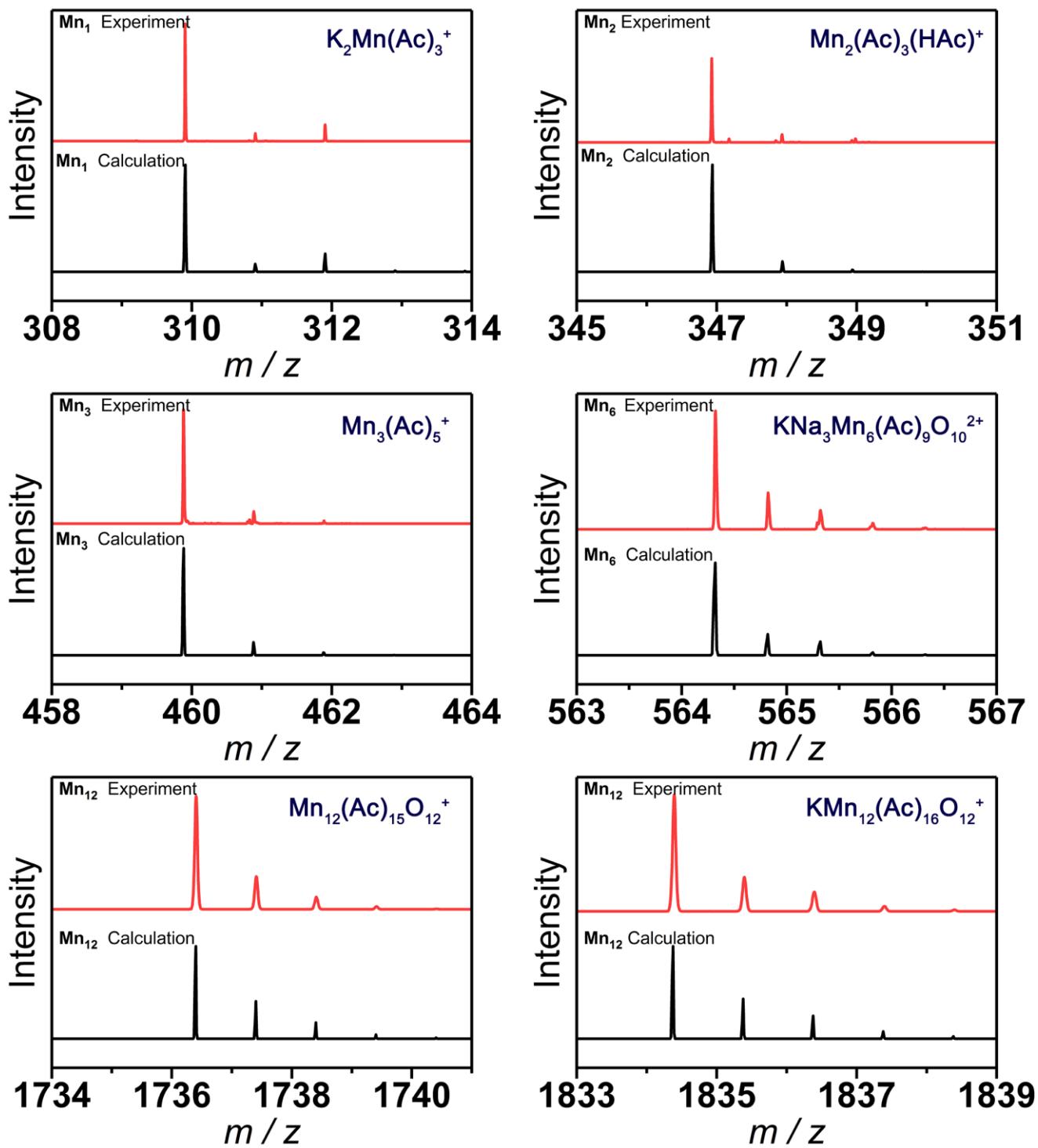


Figure S8. Selected experimental (red) and simulated (black) mass spectra of the isotopic envelopes for **sol.Mn-W** in positive mode.

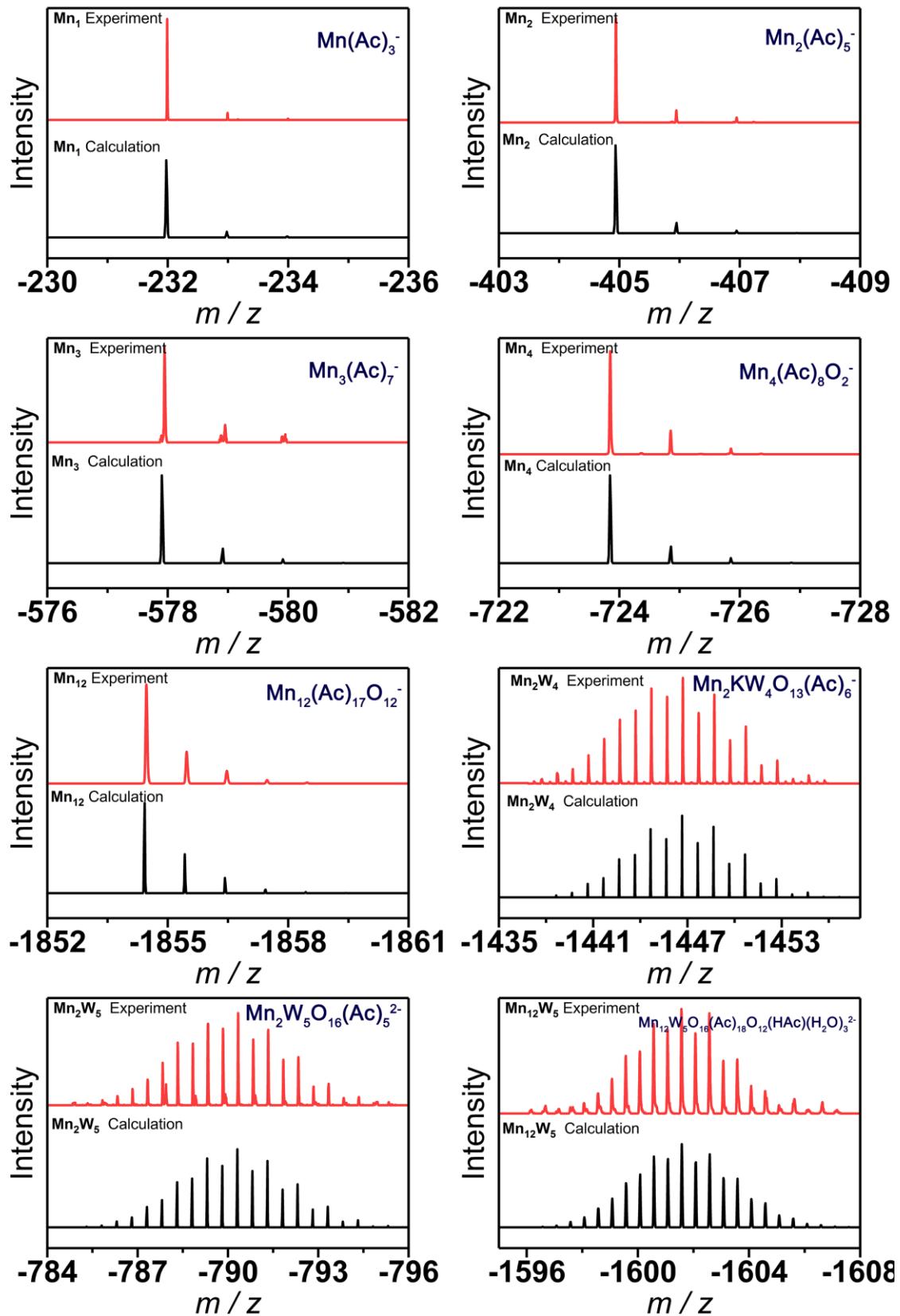


Figure S9. Selected experimental (red) and simulated (black) mass spectra of the isotopic envelopes for **sol.Mn-W** in negative mode.

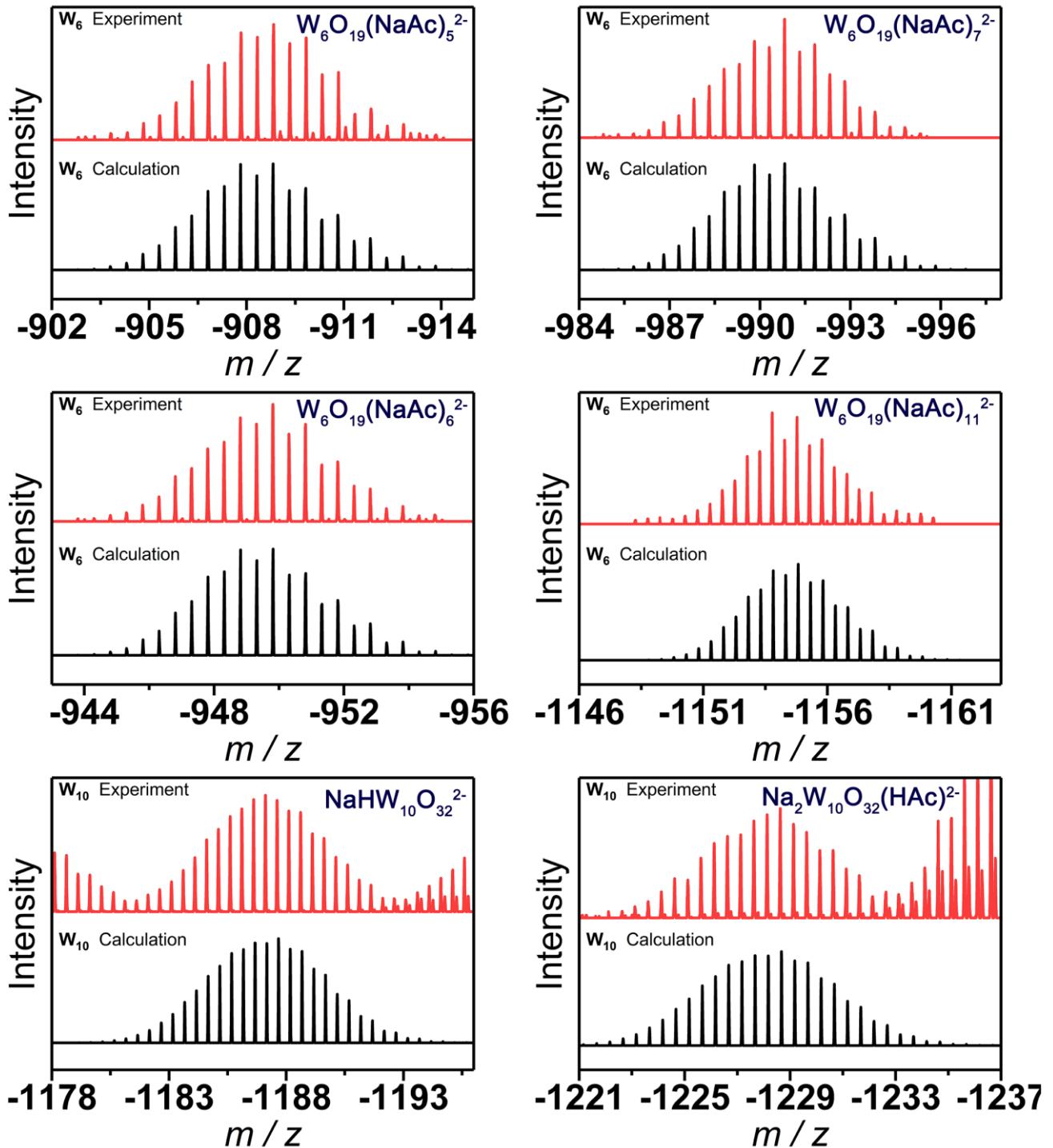


Figure S10. Selected experimental (red) and simulated (black) mass spectra of the isotopic envelopes for **sol.** HAc-W in negative mode.

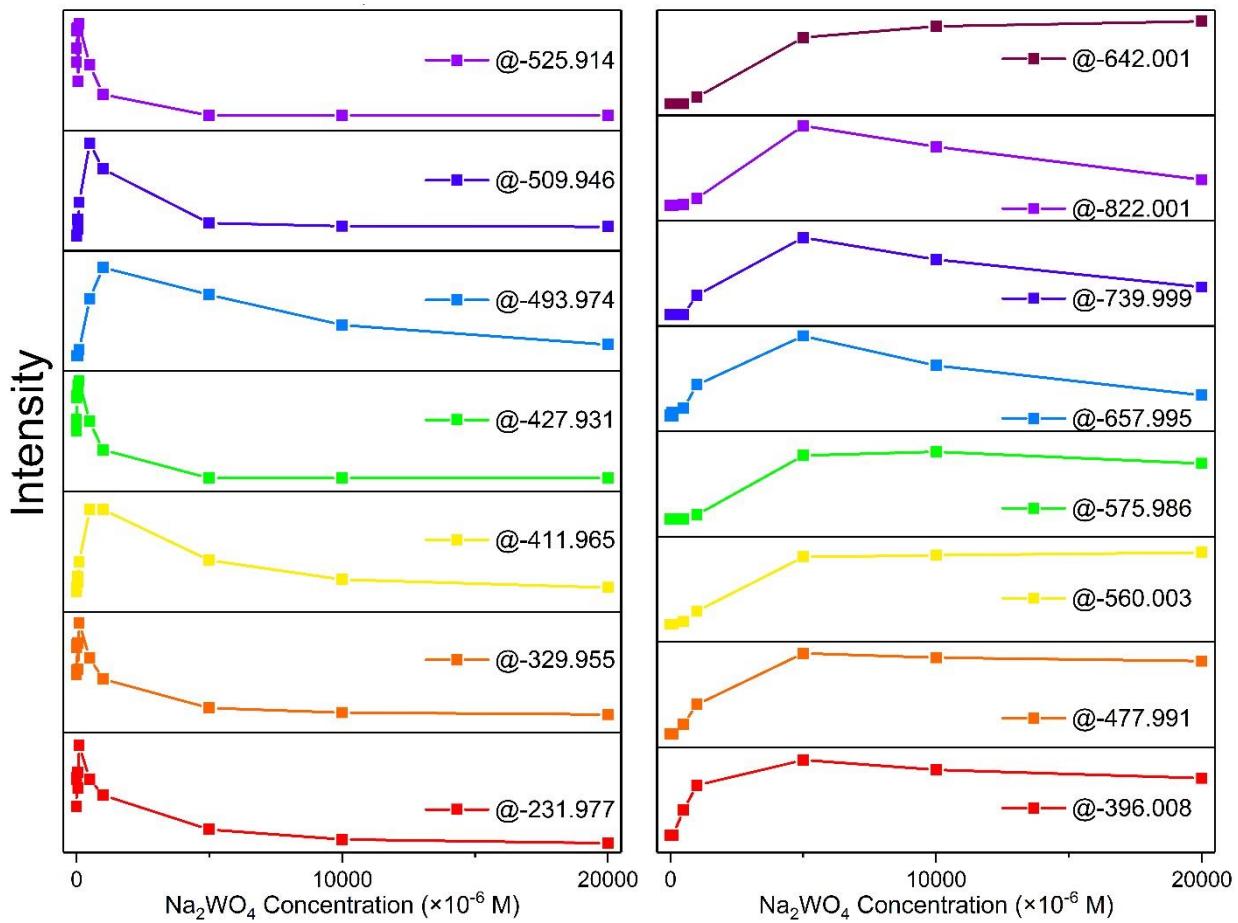


Figure S11. Negative mode of ESI-MS spectral intensity- Na_2WO_4 concentration profiles of Mn_1 species (detail see Table S4) during the synthesis process in **sol.Mn-W**.

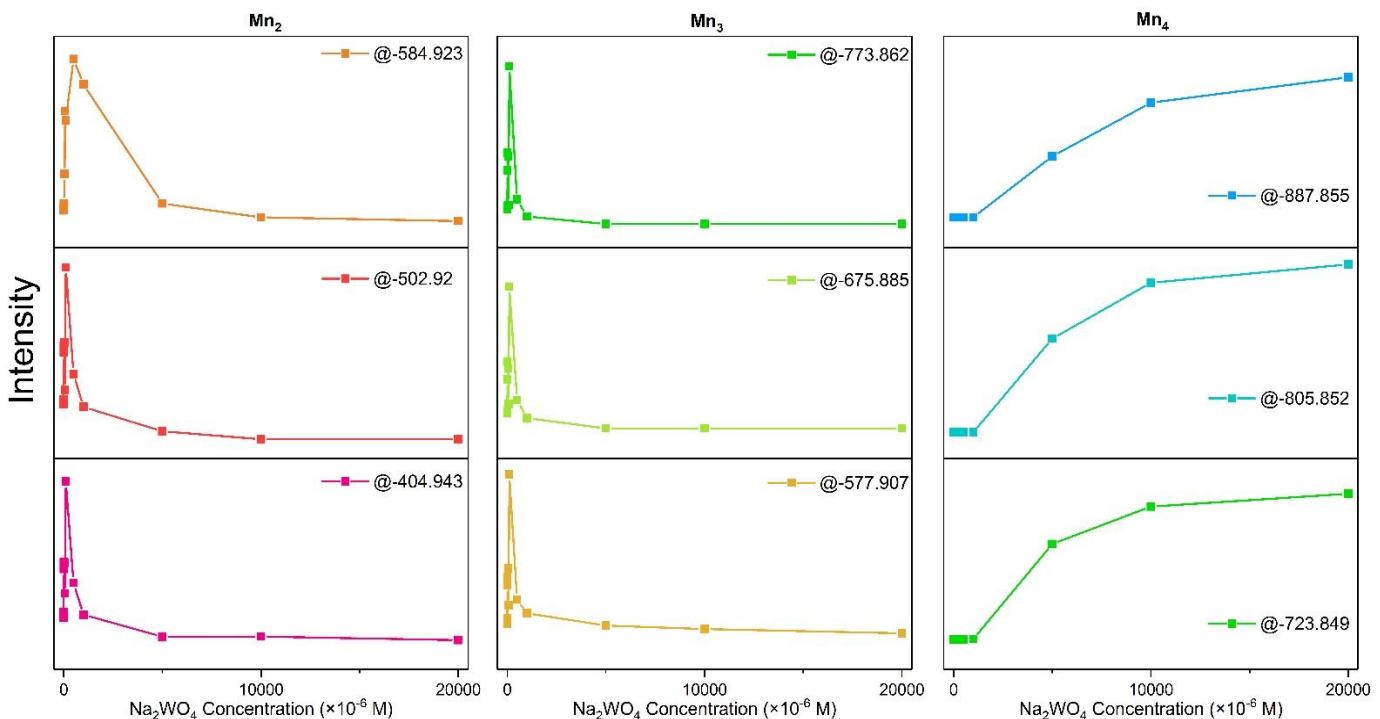


Figure S12. Negative mode of ESI-MS spectral intensity- Na_2WO_4 concentration profiles of Mn_2 , Mn_3 , and Mn_4 species (detail see Table S4) during the synthesis process in **sol.Mn-W**.

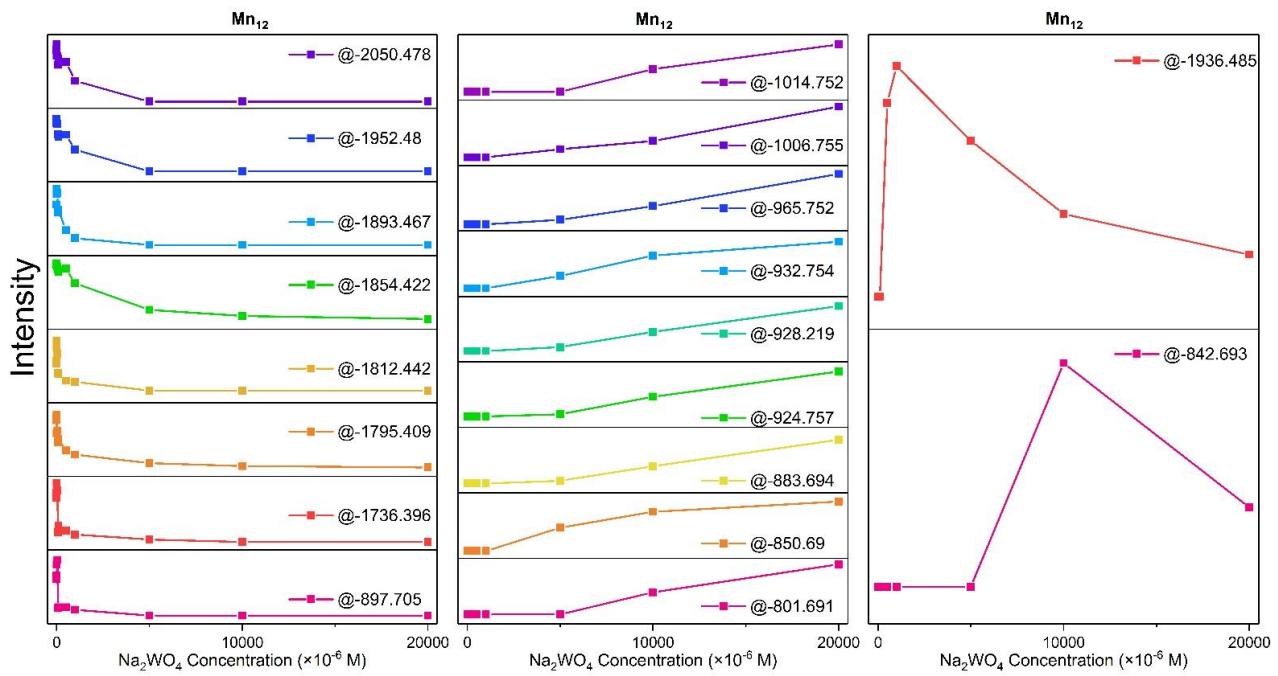


Figure S13. Negative mode of ESI-MS spectral intensity- Na_2WO_4 concentration profiles of Mn_{12} species (detail see Table S4) during the synthesis process in **sol.Mn-W**.

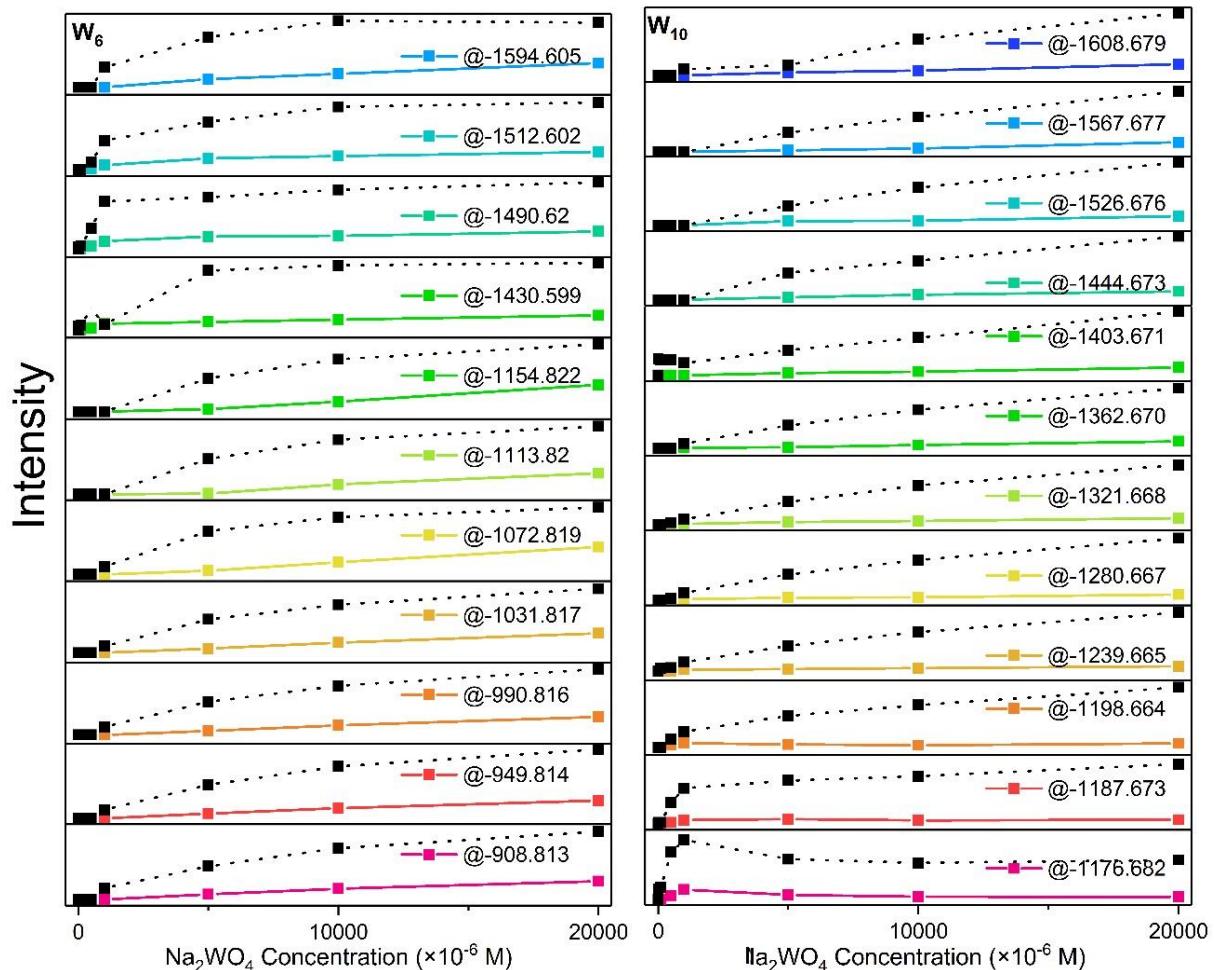


Figure S14. Negative mode of ESI-MS spectral intensity- Na_2WO_4 concentration profiles of W_6 (left) and W_{10} (right) species (detail see Table S5) during the synthesis process in **sol.Mn-W**. The black dot lines represent corresponding intensities of the species in **sol.HAc-W**.

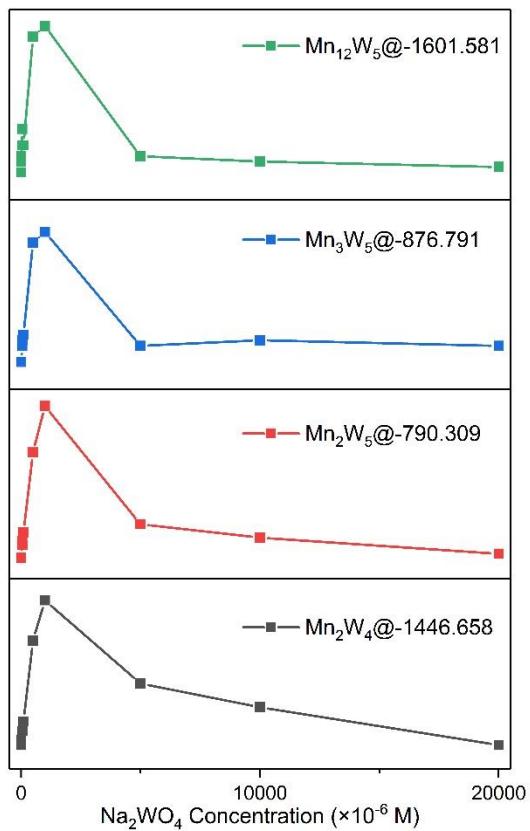


Figure S15. Negative mode of ESI-MS spectral intensity- Na_2WO_4 concentration profiles of **Mn-W** species during the synthesis process in **sol.Mn-W**.

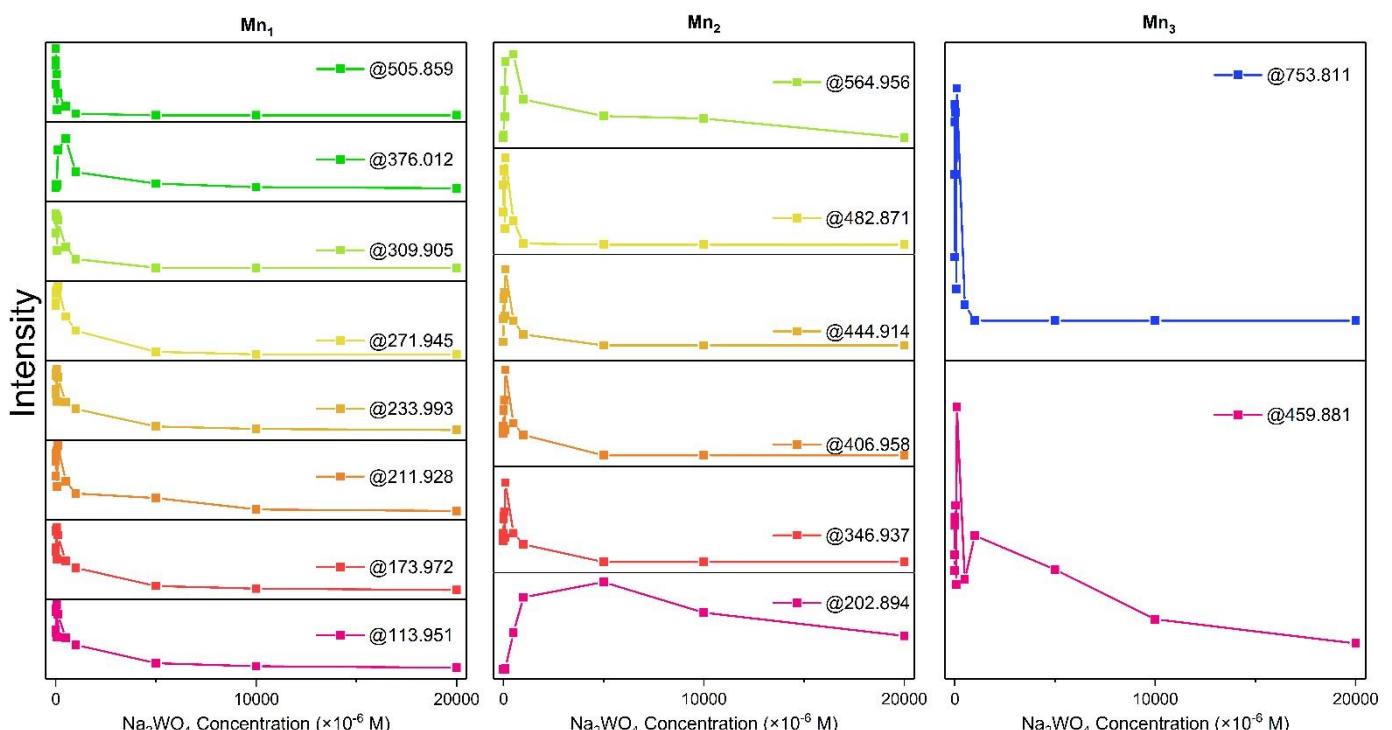


Figure S16. Positive mode of ESI-MS spectral intensity- Na_2WO_4 concentration profiles of **Mn₁**, **Mn₂**, and **Mn₃** species (detail see **Table S3**) during the synthesis process in **sol.Mn-W**.

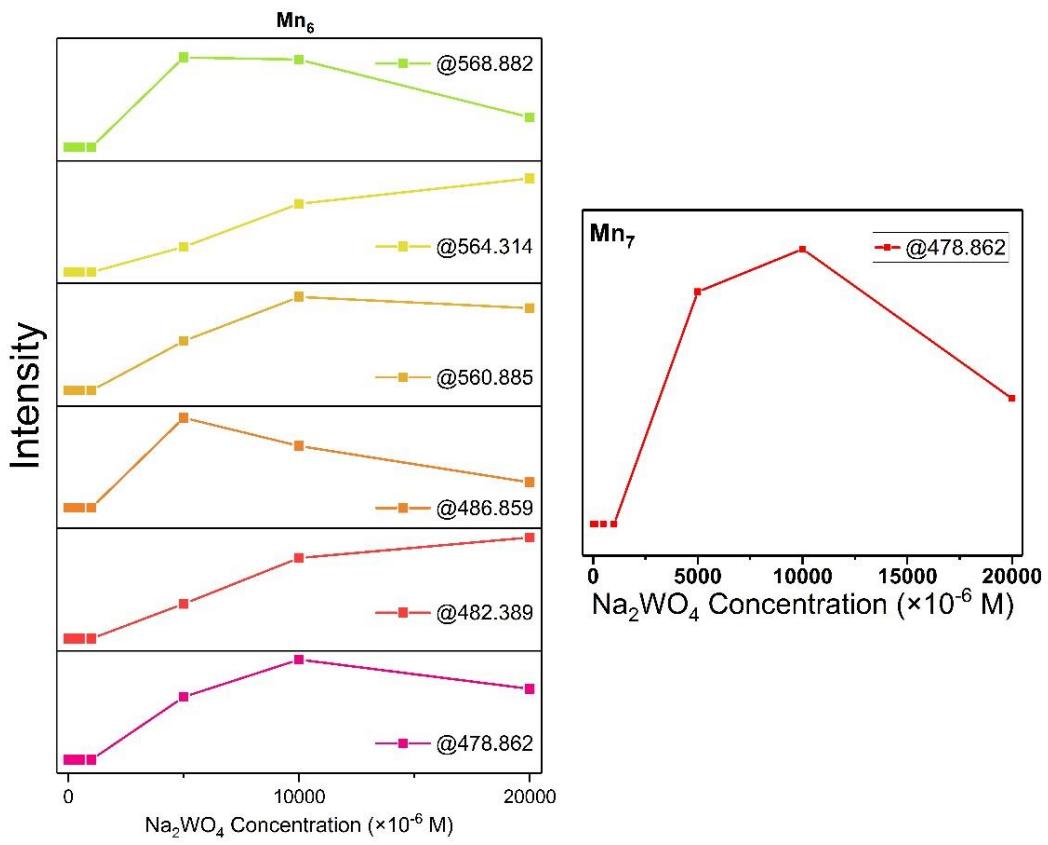


Figure S17. Positive mode of ESI-MS spectral intensity-Na₂WO₄ concentration profiles of **Mn₆** and **Mn₇** species (detail see **Table S3**) during the synthesis process in **sol.Mn-W**.

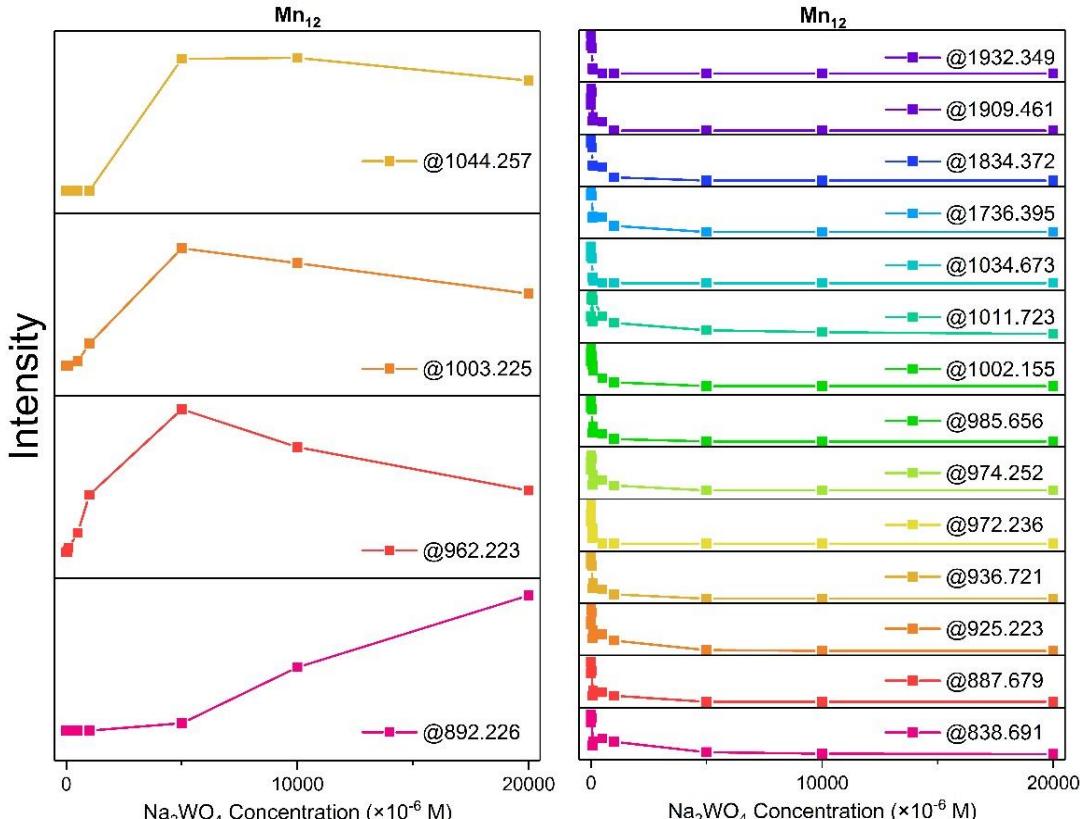


Figure S18. Positive mode of ESI-MS spectral intensity-Na₂WO₄ concentration profiles of **Mn₁₂** species (detail see **Table S3**) during the synthesis process in **sol.Mn-W**.

Table S1 Assignment of the key species identified in **sol.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
Mn₁	1	Mn(Ac) ⁺	113.951	113.954
	2	Mn(Ac)(HAc) ⁺	173.972	173.977
	3	MnK(Ac) ₂ (HAc) ⁺	271.945	271.957
	4	K ₂ Mn(Ac) ₃ ⁺	309.905	309.914
Mn₂	5	Mn ₂ (Ac) ₃ (HAc) ⁺	346.937	346.977
	6	Mn ₂ (Ac) ₃ (HAc) ₂ ⁺	406.958	406.945
	7	KMn ₂ (Ac) ₄ (HAc) ⁺	444.914	444.925
	8	K ₂ Mn ₂ (Ac) ₅ ⁺	482.871	482.884
Mn₃	9	Mn ₃ (Ac) ₅ ⁺	459.881	459.896
Mn₁₂	10	Mn ₁₂ (Ac) ₁₄ O ₁₂ ²⁺	838.691	838.718
	11	Mn ₁₂ (Ac) ₁₄ O ₁₂ (HAc) ²⁺	868.701	868.731
	12	KMn ₁₂ (Ac) ₁₅ O ₁₂ ²⁺	887.679	887.708
	13	Mn ₁₂ (Ac) ₁₆ O ₁₁ (OH)(H ₂ O) ₃ ²⁺	925.223	925.205
	14	Mn ₁₂ (Ac) ₁₆ O ₁₂ (HAc)(H ₂ O) ²⁺	936.721	936.699
	15	Mn ₁₂ (Ac) ₁₇ O ₁₂ (H ₂ O) ₅ ²⁺	972.236	972.165
	16	Mn ₁₂ (Ac) ₁₇ O ₁₀ (H ₂ O) ₇ ²⁺	974.252	974.193
	17	K ₃ Mn ₁₂ (Ac) ₁₇ O ₁₂ ²⁺	985.656	985.688
	18	K ₃ Mn ₁₂ (Ac) ₁₇ O ₁₃ (OH) ²⁺	1002.155	1002.176
	19	Mn ₁₂ (Ac) ₁₈ O ₁₄ (HAc)(H ₂ O) ²⁺	1011.723	1011.688
	20	K ₄ Mn ₁₂ (Ac) ₁₆ O ₁₀ (HAc)(H ₂ O) ₅ ²⁺	1034.673	1034.678
	21	K ₅ Mn ₁₂ (Ac) ₁₇ O ₁₀ (HAc)(H ₂ O) ₅ ²⁺	1083.662	1083.669
	22	Mn ₁₂ (Ac) ₁₅ O ₁₂ ⁺	1736.395	1736.451
	23	KMn ₁₂ (Ac) ₁₆ O ₁₂ ⁺	1834.372	1834.432
	24	Mn ₁₂ (Ac) ₁₆ O ₁₂ (HAc)(H ₂ O) ₃ ⁺	1909.461	1909.423
	25	K ₂ Mn ₁₂ (Ac) ₁₇ O ₁₂ ⁺	1932.349	1932.401
	26	K ₃ Mn ₁₂ (Ac) ₁₈ O ₁₂ ⁺	2030.326	2030.389

Table S2 Assignment of the key species identified in **sol.Mn** in the 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
Mn₁	1	Mn(Ac) ₃ ⁻	-231.977	-231.981
	2	KMn(Ac) ₄ ⁻	-329.955	-329.961
	3	K ₂ Mn(Ac) ₅ ⁻	-427.932	-427.942
Mn₂	4	Mn ₂ (Ac) ₅ ⁻	-404.943	-404.951
	5	KMn ₂ (Ac) ₆ ⁻	-502.920	-502.932
Mn₃	6	Mn ₃ (Ac) ₇ ⁻	-577.907	-577.922
	7	KMn ₃ (Ac) ₈ ⁻	-675.885	-675.904
Mn₁₂	8	Mn ₁₂ (Ac) ₁₅ O ₁₂ ⁻	-1736.396	-1736.452
	9	Mn ₁₂ (Ac) ₁₆ O ₁₂ ⁻	-1795.409	-1795.474
	10	Mn ₁₂ (Ac) ₁₅ O ₁₃ (HAc) ⁻	-1812.442	-1812.473
	11	Mn ₁₂ (Ac) ₁₇ O ₁₂ ⁻	-1854.422	-1854.486
	12	Mn ₁₂ (Ac) ₁₄ O ₁₂ (HAc) ₃ (H ₂ O) ₂ ⁻	-1893.467	-1893.452
	13	Mn ₁₂ (Ac) ₁₅ O ₁₂ (HAc) ₃ (H ₂ O) ₂ ⁻	-1952.480	-1952.469
	14	K ₃ Mn ₁₂ (Ac) ₁₈ O ₁₁ (H ₂ O) ₂ ⁻	-2050.351	-2050.367

Table S3 Assignment of the key species identified in **sol.Mn-W** 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
Mn₁	1	Mn(Ac) ⁺	113.951	113.978
	2	Mn(Ac)(HAc) ⁺	173.972	174.008
	3	KMn(Ac) ₂ ⁺	211.928	211.969
	4	Mn(Ac)(HAc) ₂ ⁺	233.993	234.038
	5	KMn(Ac) ₂ (HAc) ⁺	271.945	271.998
	6	K ₂ Mn(Ac) ₃ ⁺	309.905	309.959
	7	NaMn(Ac) ₂ (HAc) ₃ ⁺	376.012	376.041
	8	K ₄ Mn(Ac) ₅ ⁺	505.859	505.936
Mn₂	9	Mn ₂ (Ac)O(H ₂ O) ⁺	202.894	202.992
	10	Mn ₂ (Ac) ₃ (HAc) ⁺	346.937	346.995
	11	Mn ₂ (Ac) ₃ (HAc) ₂ ⁺	406.958	407.001
	12	KMn ₂ (Ac) ₄ (HAc) ⁺	444.914	444.983
	13	K ₂ Mn ₂ (Ac) ₅ ⁺	482.871	482.923
	14	KMn ₂ (Ac) ₄ (HAc) ₃ ⁺	564.956	564.959

Species	Entry	Identification	Cal.m/z	Exp.m/z
Mn₃	15	Mn ₃ (Ac) ₅ ⁺	459.881	459.952
	16	K ₃ Mn ₃ (Ac) ₈ ⁺	753.811	753.918
Mn₆	17	Mn ₆ (Ac) ₈ O ₆ (HAc) ²⁺	478.862	478.739
	18	Mn ₆ (Ac) ₅ O ₄ (HAc) ₄ (H ₂ O) ₂ ²⁺	482.389	482.251
	19	Mn ₆ (Ac) ₈ O ₇ (HAc) ²⁺	486.859	486.789
	20	KMn ₆ (Ac) ₇ O ₄ (HAc) ₄ (H ₂ O) ₂ ²⁺	560.885	560.781
	21	KNa ₃ Mn ₆ (Ac) ₉ O ₁₀ ²⁺	564.314	564.296
	22	KMn ₆ (Ac) ₇ O ₅ (HAc) ₄ (H ₂ O) ₂ ²⁺	568.882	568.773
Mn₇	23	K ₂ Mn ₇ (Ac) ₉ O ₈ (HAc) ₃ ²⁺	650.818	650.814
Mn₁₂	24	Mn ₁₂ (Ac) ₁₄ O ₁₂ ²⁺	838.691	838.731
	25	Mn ₁₂ (Ac) ₁₄ O ₁₂ (HAc) ²⁺	868.701	868.776
	26	KMn ₁₂ (Ac) ₁₅ O ₁₂ ²⁺	887.679	887.763
	27	Mn ₁₂ (Ac) ₁₅ O ₉ (H ₂ O) ₂ (HAc) ² ₊	892.226	892.301
	28	Mn ₁₂ (Ac) ₁₆ O ₁₁ (OH)(H ₂ O) ₃₂ ⁺	925.223	925.269
	29	Mn ₁₂ (Ac) ₁₆ O ₁₂ (H ₂ O)(HAc) ² ₊	936.721	936.796
	30	Mn ₁₂ (Ac) ₁₇ O ₁₃ (H ₂ O) ₃ ²⁺	962.223	962.171
	31	Mn ₁₂ (Ac) ₁₇ O ₁₂ (H ₂ O) ₅ ²⁺	972.236	972.267
	32	Mn ₁₂ (Ac) ₁₇ O ₁₀ (H ₂ O) ₇ ²⁺	974.252	974.295
	33	K ₃ Mn ₁₂ (Ac) ₁₇ O ₁₂ ²⁺	985.656	985.737
	34	K ₃ Mn ₁₂ (Ac) ₁₇ O ₁₃ (OH) ²⁺	1002.15 ₅	1002.23 ₈
	35	Mn ₁₂ Na(Ac) ₁₈ O ₁₃ (H ₂ O) ₃ ²⁺	1003.22 ₅	1003.19 ₁
	36	Mn ₁₂ (Ac) ₁₈ O ₁₄ (H ₂ O)(HAc) ² ₊	1011.72 ₃	1011.75 ₉
	37	K ₄ Mn ₁₂ (Ac) ₁₆ O ₁₀ (H ₂ O) ₅ (HA _c) ₂ ²⁺	1034.67 ₃	1034.73 ₄
	38	Mn ₁₂ (Ac) ₁₇ O ₁₂ (HAc) ₃ (H ₂ O) ₃₂ ⁺	1044.25 ₇	1044.21 ₂
	39	K ₅ Mn ₁₂ (Ac) ₁₇ O ₁₀ (H ₂ O) ₅ (HA _c) ₂ ²⁺	1083.66 ₂	1083.66 ₉
	40	Mn ₁₂ (Ac) ₁₅ O ₁₂ ⁺	1736.39 ₅	1736.44 ₆
	41	KMn ₁₂ (Ac) ₁₆ O ₁₂ ⁺	1834.37 ₂	1834.42 ₃
	42	Mn ₁₂ (Ac) ₁₆ O ₁₂ (HAc)(H ₂ O) ₃ ⁺	1909.46 ₁	1909.42 ₃
	43	K ₂ Mn ₁₂ (Ac) ₁₇ O ₁₂ ⁺	1932.34 ₉	1932.40 ₉
	44	K ₃ Mn ₁₂ (Ac) ₁₈ O ₁₂ ⁺	2030.32 ₆	2030.38 ₈

Table S4 Assignment of the key species identified in **sol.Mn-W** in the 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
Mn₁	1	Mn(Ac) ₃ ⁻	-231.977	-231.981
	2	KMn(Ac) ₄ ⁻	-329.955	-329.955
	3	Na ₂ Mn(Ac) ₅ ⁻	-396.012	-396.008
	4	NaKMn(Ac) ₅ ⁻	-411.959	-411.965
	5	K ₂ Mn(Ac) ₅ ⁻	-427.932	-427.931
	6	Na ₃ Mn(Ac) ₆ ⁻	-477.988	-477.991
	7	Na ₂ KMn(Ac) ₆ ⁻	-493.962	-493.974
	8	NaK ₂ Mn(Ac) ₆ ⁻	-509.935	-509.946
	9	K ₃ Mn(Ac) ₆ ⁻	-525.909	-525.914
	10	Na ₄ Mn(Ac) ₇ ⁻	-599.991	-560.003
	11	Na ₃ KMn(Ac) ₇ ⁻	-575.964	-575.986
	12	Na ₄ KMn(Ac) ₈ ⁻	-657.967	-657.995
	13	Na ₅ KMn(Ac) ₉ ⁻	-739.971	-739.999
	14	Na ₆ KMn(Ac) ₁₀ ⁻	-821.974	-822.001
	15	Na ₅ Mn(Ac) ₈ ⁻	-641.994	-642.001
Mn₂	16	Mn ₂ (Ac) ₅ ⁻	-404.943	-404.947
	17	KMn ₂ (Ac) ₆ ⁻	-502.920	502.941
	18	NaKMn ₂ (Ac) ₇ ⁻	-584.923	-584.934
Mn₃	19	Mn ₃ (Ac) ₇ ⁻	-577.907	-577.930
	20	KMn ₃ (Ac) ₈ ⁻	-675.885	-675.896
	21	K ₂ Mn ₃ (Ac) ₉ ⁻	-773.862	-773.898
Mn₄	22	NaMn ₄ (Ac) ₉ O ₂ ⁻	-805.852	-805.871
	23	Na ₂ Mn ₄ (Ac) ₁₀ O ₂ ⁻	-887.855	-887.885
	24	Mn ₄ (Ac) ₈ O ₂ ⁻	-723.849	-723.866
Mn₁₂	25	Mn ₁₂ (Ac) ₁₂ O ₁₁ (HAc) ²⁻	-801.691	-801.627
	26	NaMn ₁₂ (Ac) ₁₃ O ₁₁ (HAc) ²⁻	-842.693	-842.636
	27	NaMn ₁₂ (Ac) ₁₃ O ₁₂ (HAc) ²⁻	-850.690	-850.675
	28	Na ₂ Mn ₁₂ (Ac) ₁₄ O ₁₁ (HAc) ²⁻	-883.694	-883.655
	29	Mn ₁₂ (Ac) ₁₆ O ₁₂ ²⁻	-897.705	-897.697
	30	Mn ₁₂ (Ac) ₁₆ O ₆ (HAc)(H ₂ O) ₅ ²⁻	-924.757	-924.758
	31	Mn ₁₂ (Ac) ₁₇ O ₁₁ (H ₂ O) ²⁻	-928.219	-928.199
	32	Mn ₁₂ (Ac) ₁₆ O ₇ (HAc)(H ₂ O) ₅ ²⁻	-932.754	-932.746
	33	Mn ₁₂ (Ac) ₁₆ O ₁₀ (HAc)(H ₂ O) ₆ ²⁻	-965.752	-965.771
	34	Mn ₁₂ (Ac) ₁₄ O ₁₂ (HAc) ₅ (H ₂ O) ₂ ²⁻	-1006.755	-1006.777
	35	Mn ₁₂ (Ac) ₁₆ O ₁₂ (HAc) ₃ (H ₂ O) ₃ ²⁻	-1014.752	-1014.766

Species	Entry	Identification	Cal.m/z	Exp.m/z
	36	Mn ₁₂ (Ac) ₁₅ O ₁₂ ⁻	-1736.396	-1736.380
	37	Mn ₁₂ (Ac) ₁₆ O ₁₂ ⁻	-1795.409	-1795.456
	38	Mn ₁₂ (Ac) ₁₅ O ₁₃ (HAc) ⁻	-1812.442	-1812.418
	39	Mn ₁₂ (Ac) ₁₇ O ₁₂ ⁻	-1854.422	-1854.450
	40	NaMn ₁₂ (Ac) ₁₇ O ₁₂ ⁻	-1877.412	-1877.475
	41	Mn ₁₂ (Ac) ₁₄ O ₁₂ (HAc) ₃ (H ₂ O) ₂ ⁻	-1893.467	-1893.498
	42	Mn ₁₂ (Ac) ₁₅ O ₁₁ (HAc) ₃ (H ₂ O) ₂ ⁻	-1936.485	-1936.428
	43	Mn ₁₂ (Ac) ₁₅ O ₁₂ (HAc) ₃ (H ₂ O) ₂ ⁻	-1952.480	-1952.499
	44	NaMn ₁₂ (Ac) ₁₈ O ₁₂ (HAc)(H ₂ O) ₃ ⁻	-2050.478	-2050.490
Mn₁₂W₅	45	Mn ₁₂ (Ac) ₁₈ O ₁₂ (HAc)(H ₂ O) ₃ W ₅ O ₁ ₆ ²⁻	-1601.581	-1601.564
Mn₃W₅	46	Mn ₃ (Ac) ₇ W ₅ O ₁₆ ²⁻	-876.791	-876.804
Mn₂W₄	47	KMn ₂ (Ac) ₆ W ₄ O ₁₃ ⁻	-1446.658	-1446.695
Mn₂W₅	48	Mn ₂ (Ac) ₅ W ₅ O ₁₆ ²⁻	-790.309	-790.339
W₆	49	W ₆ O ₁₉ (NaAc) ₅ ²⁻	-908.813	-908.849
	50	W ₆ O ₁₉ (NaAc) ₆ ²⁻	-949.814	-949.849
	51	W ₆ O ₁₉ (NaAc) ₇ ²⁻	-990.816	-990.861
	52	W ₆ O ₁₉ (NaAc) ₈ ²⁻	-1031.817	-1031.860
	53	W ₆ O ₁₉ (NaAc) ₉ ²⁻	-1072.819	-1072.835
	54	W ₆ O ₁₉ (NaAc) ₁₀ ²⁻	-1113.820	-1113.892
	55	W ₆ O ₁₉ (NaAc) ₁₁ ²⁻	-1154.822	-1154.895
	56	NaW ₆ O ₁₉ ⁻	-1430.599	-1430.545
	57	HW ₆ O ₁₉ (NaAc) ⁻	-1490.620	-1490.692
	58	NaW ₆ O ₁₉ (NaAc) ⁻	-1512.602	-1512.665
	59	NaW ₆ O ₁₉ (NaAc) ₂ ⁻	-1594.605	-1594.677
W₁₀	60	H ₂ W ₁₀ O ₃₂ ²⁻	-1176.682	-1176.638
	61	NaHW ₁₀ O ₃₂ ²⁻	-1187.673	-1187.623
	62	Na ₂ W ₁₀ O ₃₂ ²⁻	-1198.664	-1198.616
	63	Na ₂ W ₁₀ O ₃₂ (NaAc) ²⁻	-1239.665	-1239.661
	64	Na ₂ W ₁₀ O ₃₂ (NaAc) ₂ ²⁻	-1280.667	-1280.667
	65	Na ₂ W ₁₀ O ₃₂ (NaAc) ₃ ²⁻	-1321.668	-1231.688
	66	Na ₂ W ₁₀ O ₃₂ (NaAc) ₄ ²⁻	-1362.670	-1362.683
	67	Na ₂ W ₁₀ O ₃₂ (NaAc) ₅ ²⁻	-1403.671	-1403.676
	68	Na ₂ W ₁₀ O ₃₂ (NaAc) ₆ ²⁻	-1444.673	-1444.644
	69	Na ₂ W ₁₀ O ₃₂ (NaAc) ₈ ²⁻	-1526.676	-1526.640
	70	Na ₂ W ₁₀ O ₃₂ (NaAc) ₉ ²⁻	-1567.677	-1567.643
	71	Na ₂ W ₁₀ O ₃₂ (NaAc) ₁₀ ²⁻	-1608.679	-1608.655

Table S5 Assignment of the key species identified in **sol.HAc-W** in the 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
W₆	1	W ₆ O ₁₉ ²⁻	-703.806	-703.779
	2	W ₆ O ₁₉ (NaAc)(HAc) ₂ (H ₂ O) ₃ ²⁻	-831.845	-831.799
	3	W ₆ O ₁₉ (NaAc) ₃ (H ₂ O) ₂ ²⁻	-844.821	-844.789
	4	W ₆ O ₁₉ (HAc) ₄ (H ₂ O) ₅ ²⁻	-868.875	-868.852
	5	W ₆ O ₁₉ (NaAc) ₂ (HAc) ₂ (H ₂ O) ₄ ²⁻	-881.851	-881.802
	6	W ₆ O ₁₉ (NaAc) ₆ ²⁻	-949.814	-949.851
	7	W ₆ O ₁₉ (NaAc) ₇ ²⁻	-990.816	-990.853-
	8	W ₆ O ₁₉ (NaAc) ₈ ²⁻	-1031.817	-1031.876
	9	W ₆ O ₁₉ (NaAc) ₉ ²⁻	-1072.819	-1072.856
	10	W ₆ O ₁₉ (NaAc) ₁₀ ²⁻	-1113.820	-1113.888
	11	W ₆ O ₁₉ (NaAc) ₁₁ ²⁻	-1154.822	-1154.890
	12	NaW ₆ O ₁₉ ⁻	-1430.599	-1430.568
	13	HW ₆ O ₁₉ (NaAc) ⁻	-1490.620	-1490.693
	14	NaW ₆ O ₁₉ (NaAc) ⁻	-1512.602	-1512.660
	15	NaW ₆ O ₁₉ (NaAc) ₂ ⁻	-1594.605	-1594.656
W₁₀	16	H ₂ W ₁₀ O ₃₂ ²⁻	-1176.682	-1176.621
	17	NaHW ₁₀ O ₃₂ ²⁻	-1187.673	-1187.644
	18	Na ₂ W ₁₀ O ₃₂ ²⁻	-1198.664	-1198.676
	19	Na ₂ W ₁₀ O ₃₂ (NaAc) ²⁻	-1239.665	-1239.687
	20	Na ₂ W ₁₀ O ₃₂ (NaAc) ₂ ²⁻	-1280.667	-1280.647
	21	Na ₂ W ₁₀ O ₃₂ (NaAc) ₃ ²⁻	-1321.668	-1321.634
	22	Na ₂ W ₁₀ O ₃₂ (NaAc) ₄ ²⁻	-1362.670	-1362.699
	23	Na ₂ W ₁₀ O ₃₂ (NaAc) ₅ ²⁻	-1403.671	-1403.683
	24	Na ₂ W ₁₀ O ₃₂ (NaAc) ₆ ²⁻	-1444.673	-1444.629
	25	Na ₂ W ₁₀ O ₃₂ (NaAc) ₈ ²⁻	-1526.676	-1526.652
	26	Na ₂ W ₁₀ O ₃₂ (NaAc) ₉ ²⁻	-1567.677	-1567.630
	27	Na ₂ W ₁₀ O ₃₂ (NaAc) ₁₀ ²⁻	-1608.679	-1608.639