Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary information for:

Niobium uptake by $[P_8W_{48}O_{184}]^{40-}$ macrocyclic polyanion

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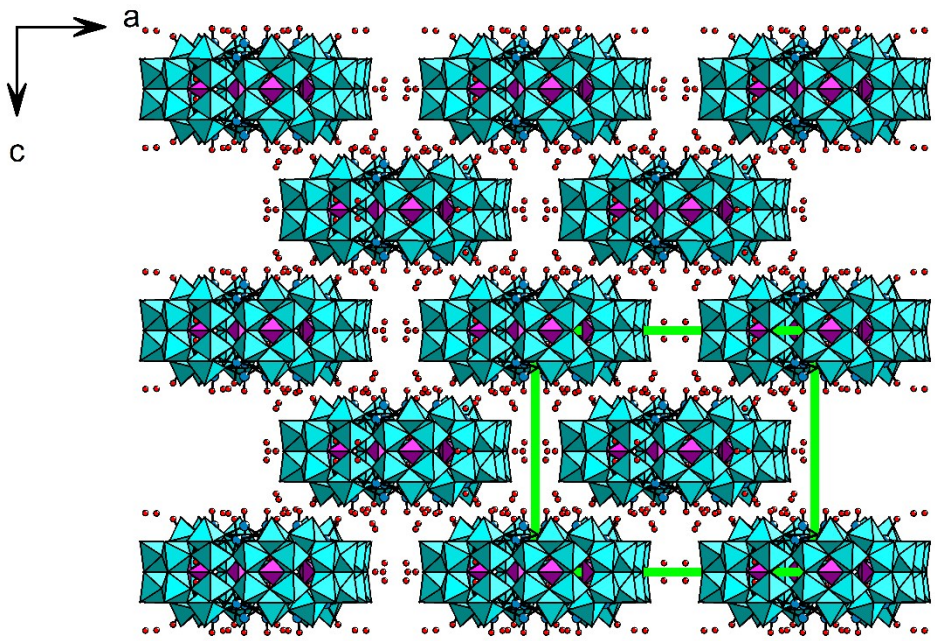
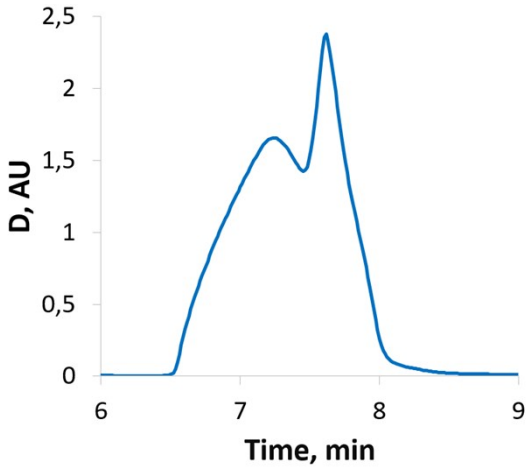
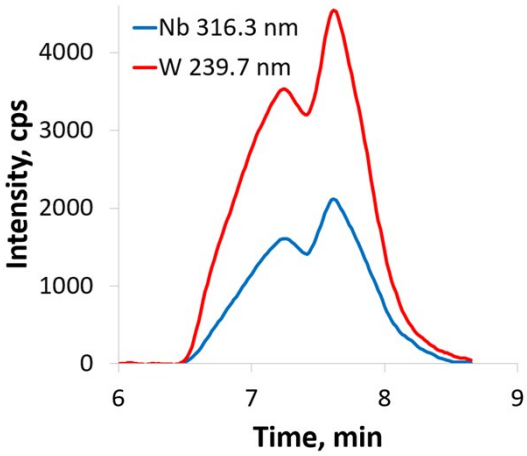
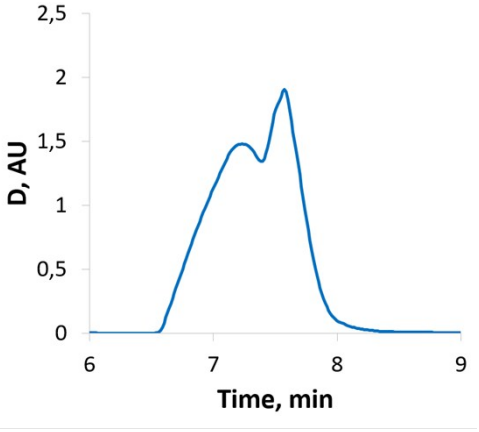


Fig. S1. Crystal packing of **1**.


D, AU
Time, min


Nb 316.3 nm
W 239.7 nm
Intensity, cps
Time, min

a)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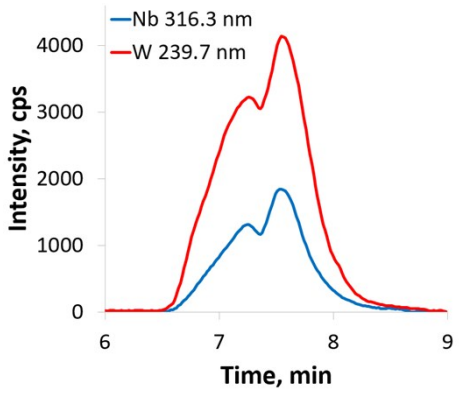
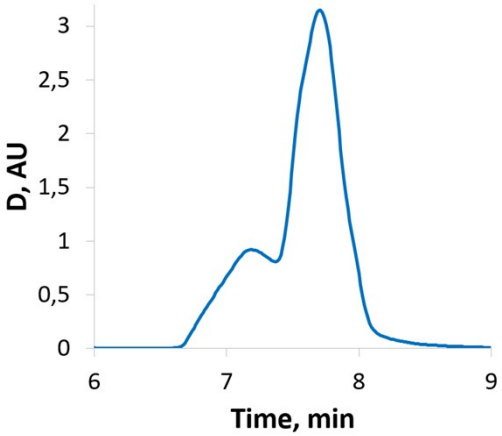
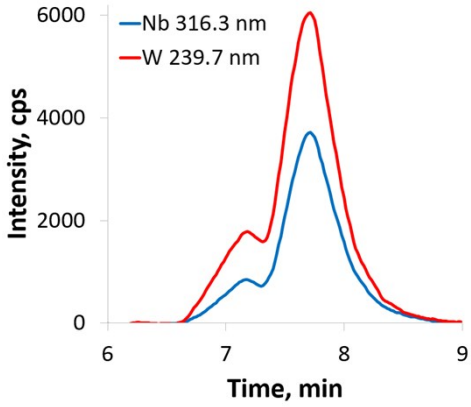
Time, min

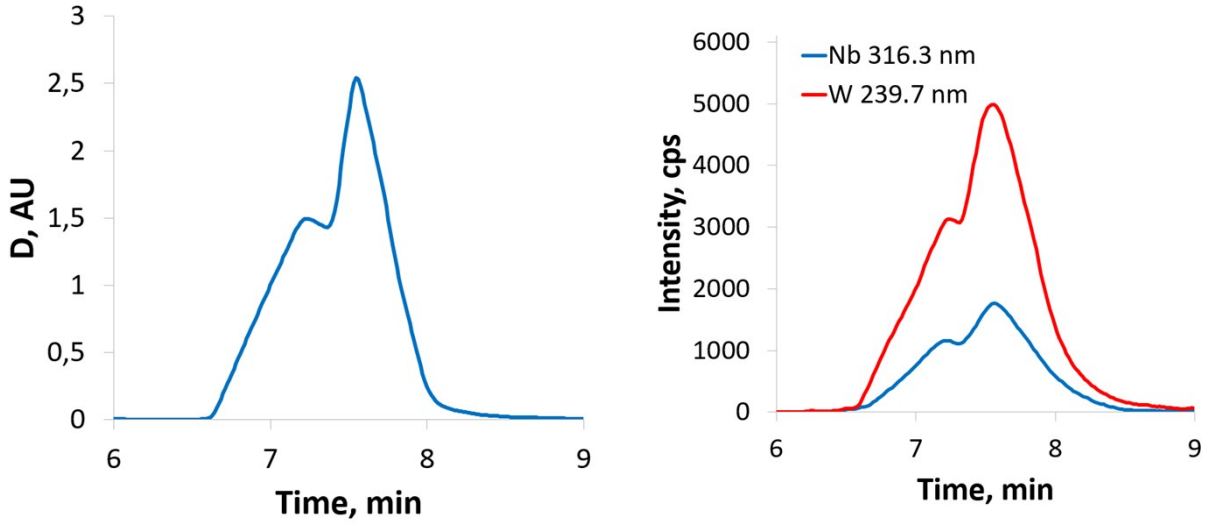

Nb 316.3 nm
W 239.7 nm
Intensity, cps
Time, min

b)

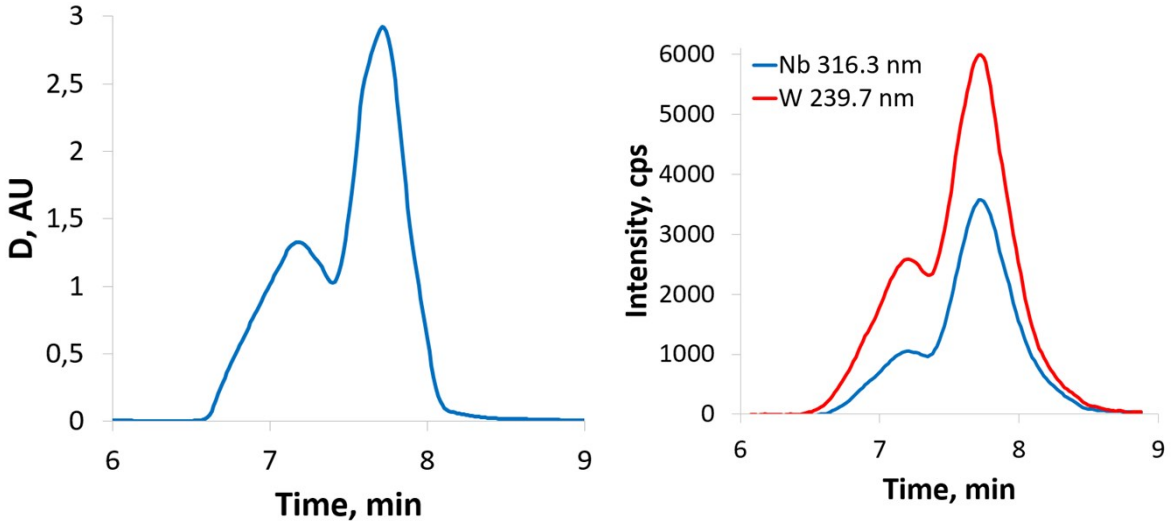

D, AU
Time, min


Nb 316.3 nm
W 239.7 nm
Intensity, cps
Time, min

c)



d)



e)

Fig. S2. HPLC-UV (left) and HPLC-ICP-AES (right) chromatograms of **A(a-e)**.

Table S1. Retention times for peaks observed by HPLC-ICP-AES for **A** and **B**.

Compound	Reference	Peak №1, Time, min	Peak № 2 Time, min
A(a)	Fig. S2 a	6,733	7,103
A(b)	Fig. S2 b	6,732	7,061
A(c)	Fig. S2 c	6,678	7,184
A(d)	Fig. S2 d	6,718	7,033
A(e)	Fig. S2 e	6,678	7,198
B(a)	Fig. 4 a	6,496	6,779
B(b)	Fig. 4 b	6,576	6,810
B(c)	Fig. 4 c	6,980	7,263
B(d)	Fig. 4 d	6,898	7,254

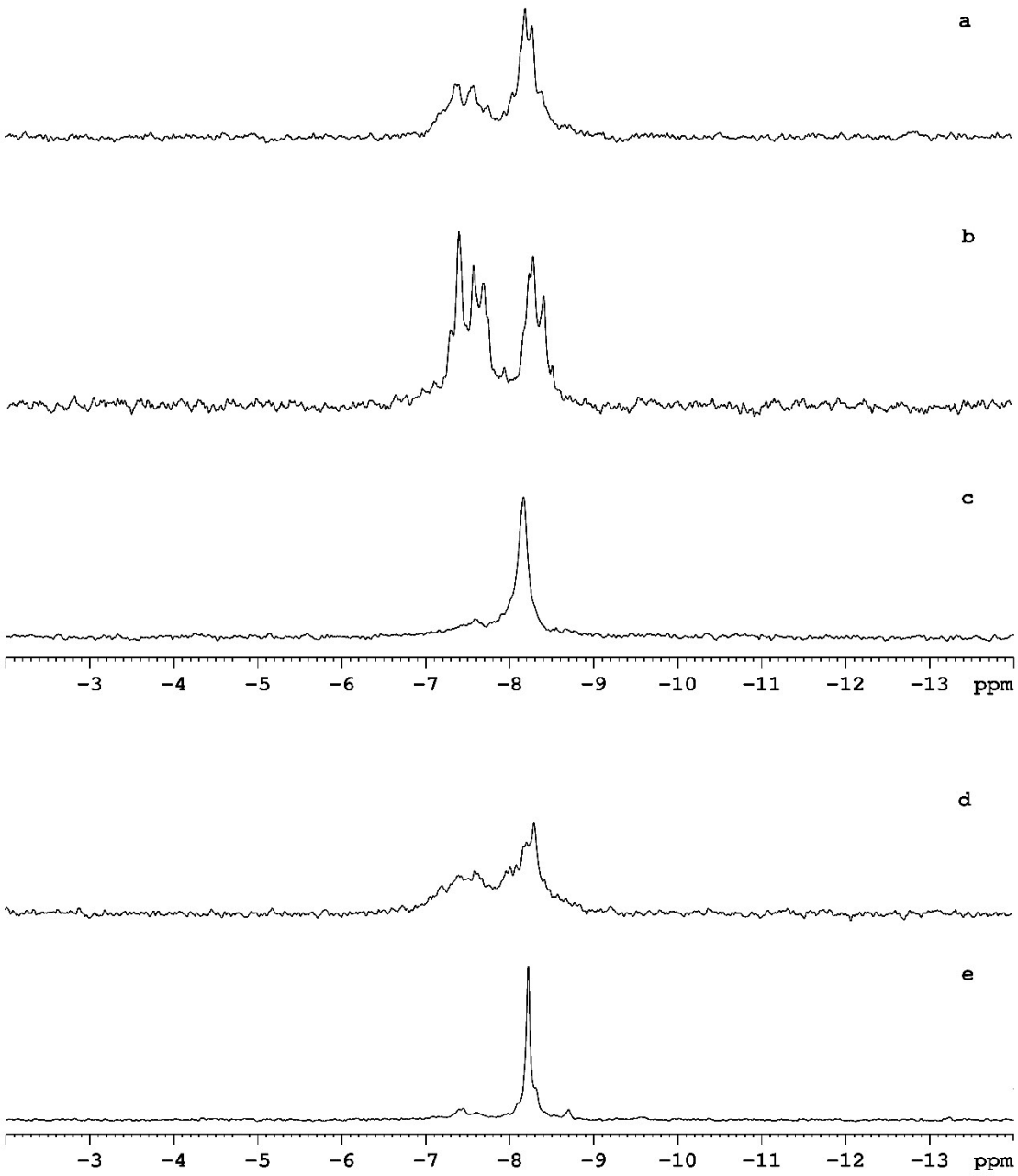


Fig. S3. ^{31}P NMR spectra for K^+/Li^+ set of Nb functionalized complexes.

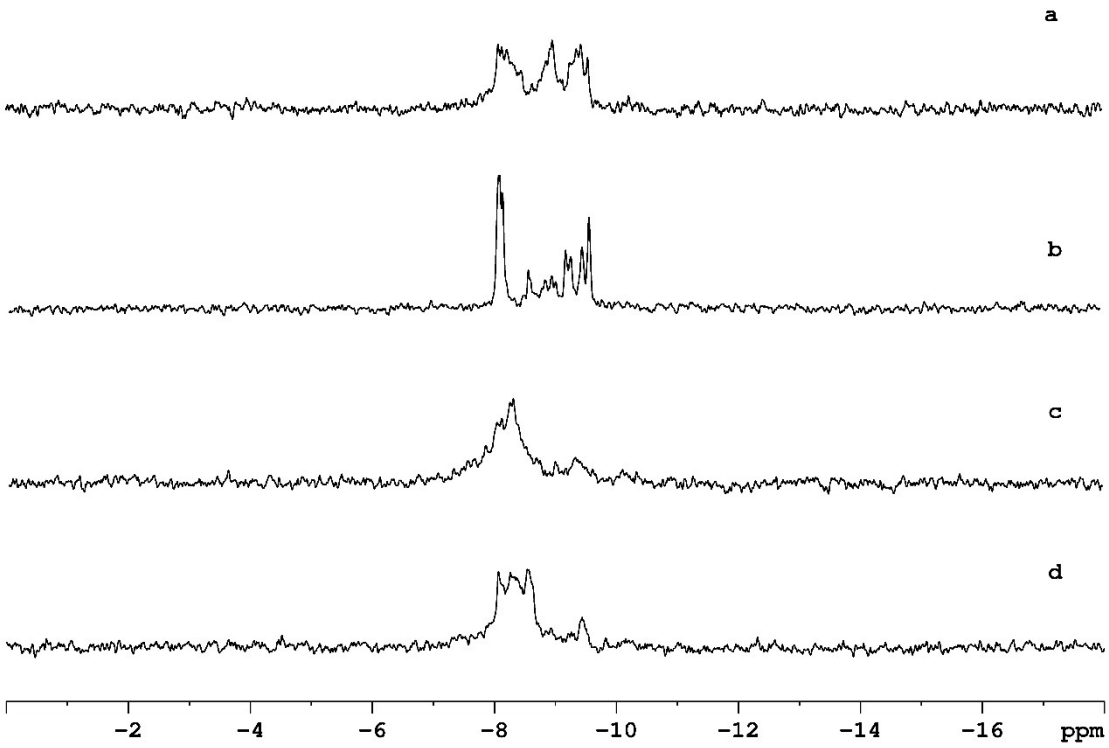


Fig. S4. ^{31}P NMR spectra for NH_4^+/Li^+ set of Nb functionalized complexes.

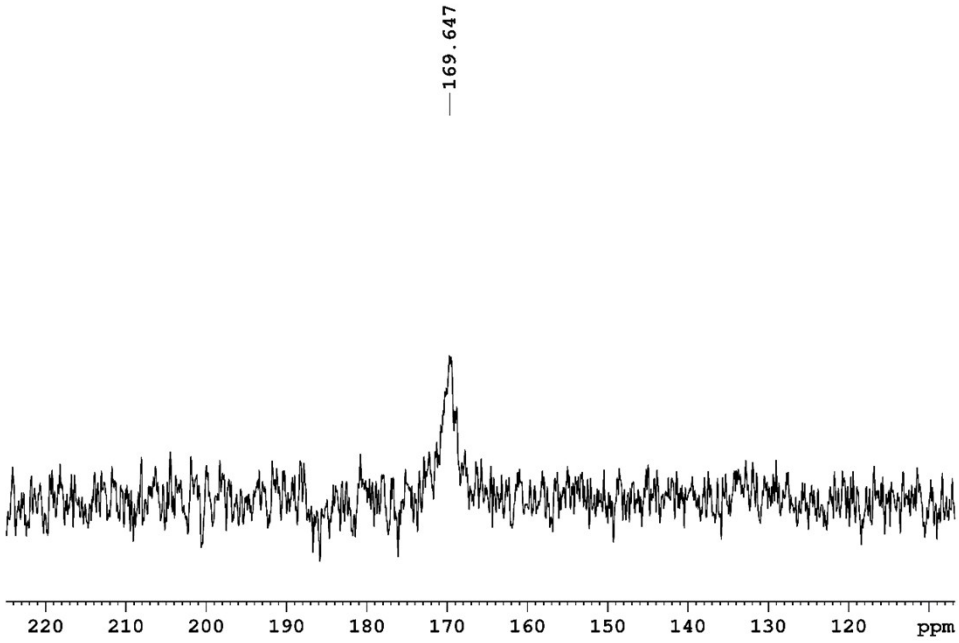


Fig. S5. Typical ^{13}C NMR spectrum for Nb functionalized $\{P_8W_{48}\}$ anions in aqueous solution.

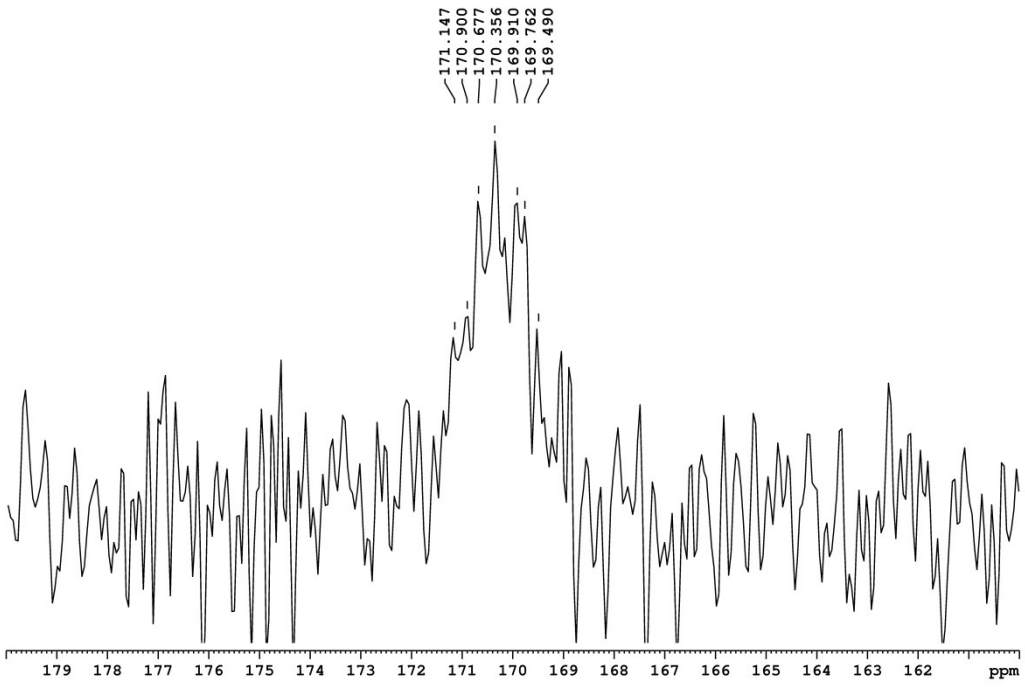


Fig. S6. Typical ^{13}C MAS NMR spectrum for Nb functionalized $\{P_8W_{48}\}$ anions in solid state.

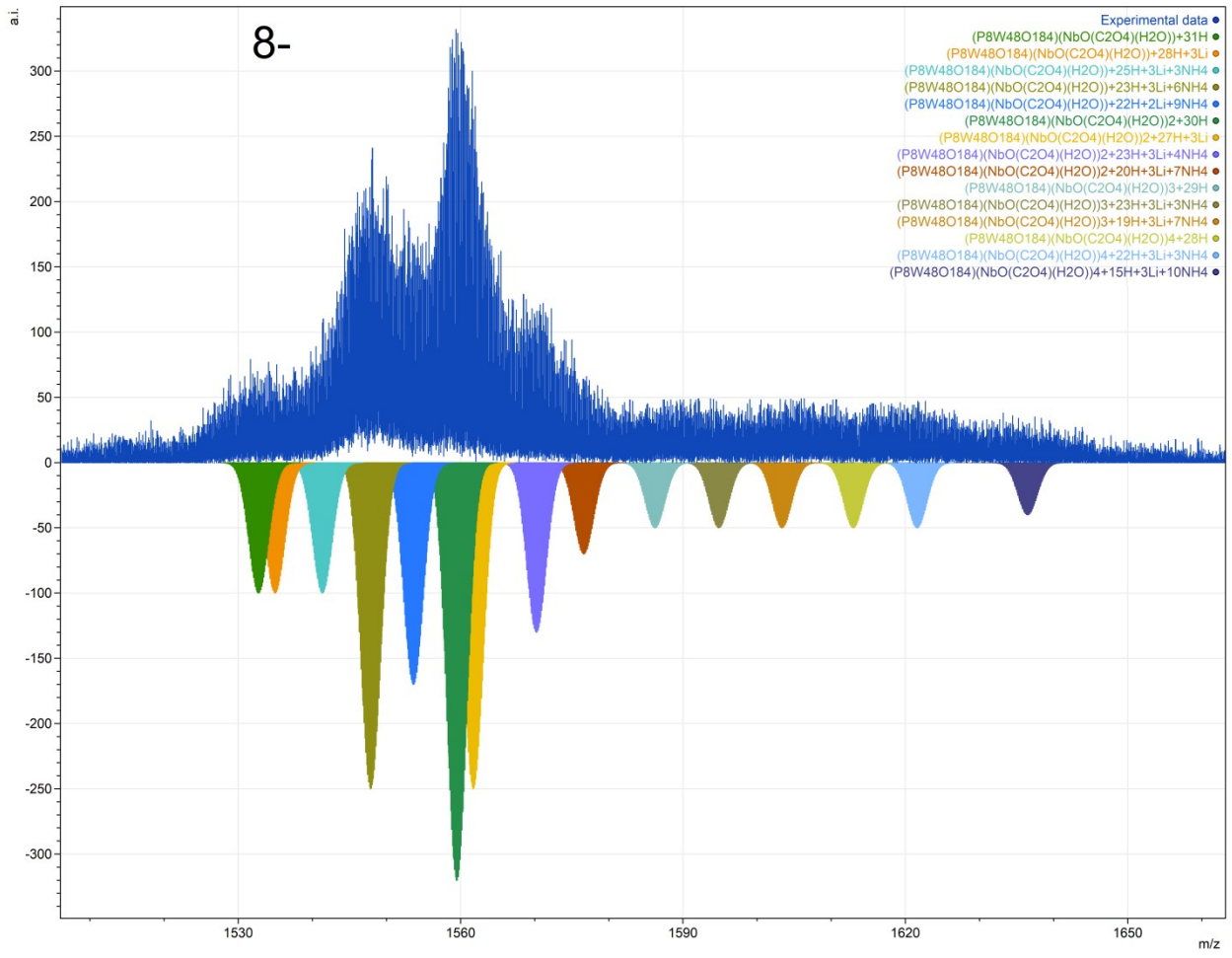

8-
a.i.
Experimental data
(P8W48O184)(NbO(C2O4)(H2O))+31H
(P8W48O184)(NbO(C2O4)(H2O))+28H+3Li
(P8W48O184)(NbO(C2O4)(H2O))+25H+3Li+3NH4
(P8W48O184)(NbO(C2O4)(H2O))+23H+3Li+6NH4
(P8W48O184)(NbO(C2O4)(H2O))+22H+2Li+9NH4
(P8W48O184)(NbO(C2O4)(H2O))2+30H
(P8W48O184)(NbO(C2O4)(H2O))2+27H+3Li
(P8W48O184)(NbO(C2O4)(H2O))2+23H+3Li+4NH4
(P8W48O184)(NbO(C2O4)(H2O))2+20H+3Li+7NH4
(P8W48O184)(NbO(C2O4)(H2O))3+29H
(P8W48O184)(NbO(C2O4)(H2O))3+23H+3Li+3NH4
(P8W48O184)(NbO(C2O4)(H2O))3+19H+3Li+7NH4
(P8W48O184)(NbO(C2O4)(H2O))4+28H
(P8W48O184)(NbO(C2O4)(H2O))4+22H+3Li+3NH4
(P8W48O184)(NbO(C2O4)(H2O))4+15H+3Li+10NH4
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
1530
1560
1590
1620
1650
m/z

Fig. S7.

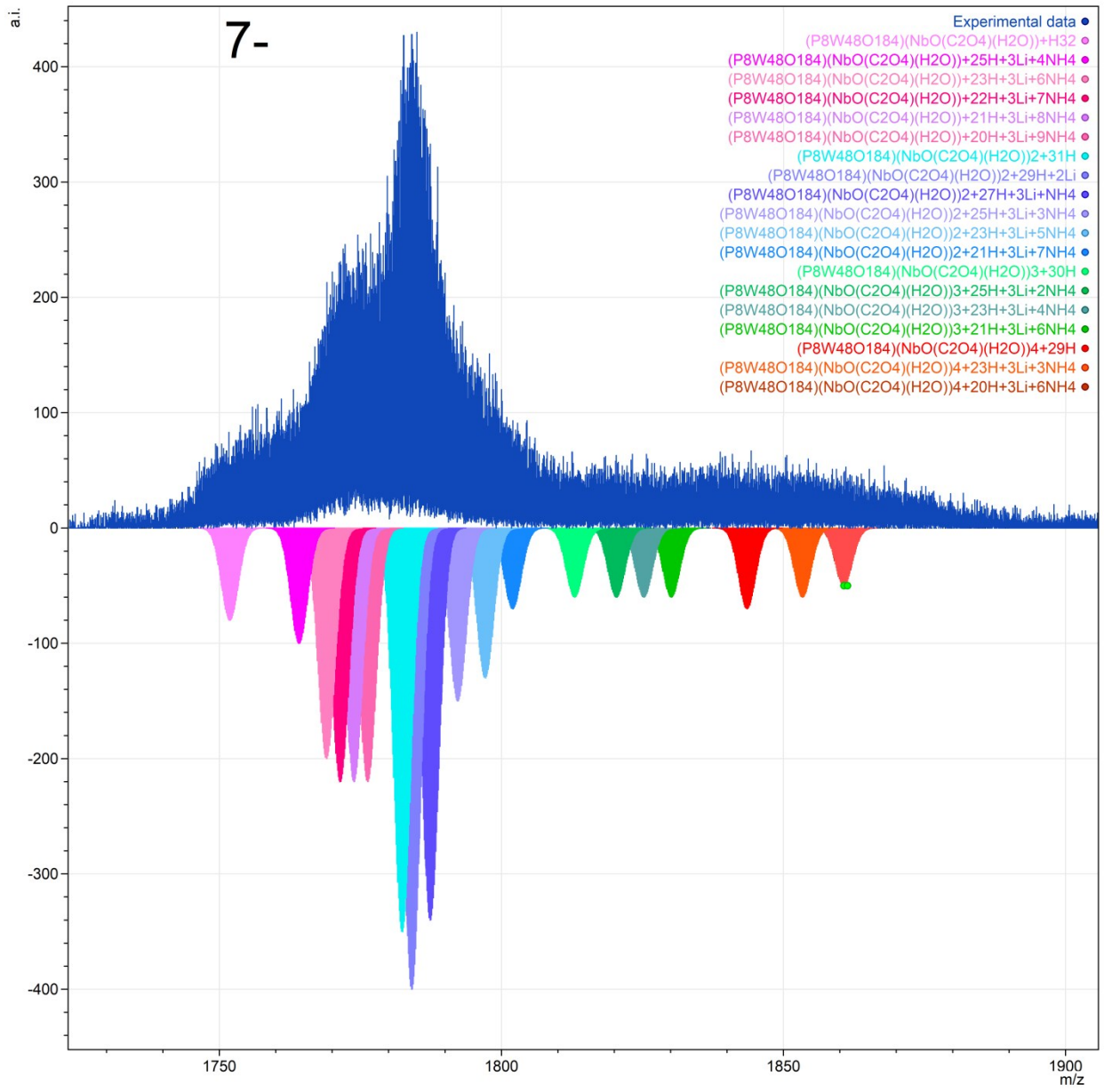

7-
a.i.
Experimental data
(P8W48O184)(NbO(C2O4)(H2O))+H32
(P8W48O184)(NbO(C2O4)(H2O))+25H+3Li+4NH4
(P8W48O184)(NbO(C2O4)(H2O))+23H+3Li+6NH4
(P8W48O184)(NbO(C2O4)(H2O))+22H+3Li+7NH4
(P8W48O184)(NbO(C2O4)(H2O))+21H+3Li+8NH4
(P8W48O184)(NbO(C2O4)(H2O))+20H+3Li+9NH4
(P8W48O184)(NbO(C2O4)(H2O))2+31H
(P8W48O184)(NbO(C2O4)(H2O))2+29H+2Li
(P8W48O184)(NbO(C2O4)(H2O))2+27H+3Li+NH4
(P8W48O184)(NbO(C2O4)(H2O))2+25H+3Li+3NH4
(P8W48O184)(NbO(C2O4)(H2O))2+23H+3Li+5NH4
(P8W48O184)(NbO(C2O4)(H2O))2+21H+3Li+7NH4
(P8W48O184)(NbO(C2O4)(H2O))3+30H
(P8W48O184)(NbO(C2O4)(H2O))3+25H+3Li+2NH4
(P8W48O184)(NbO(C2O4)(H2O))3+23H+3Li+4NH4
(P8W48O184)(NbO(C2O4)(H2O))3+21H+3Li+6NH4
(P8W48O184)(NbO(C2O4)(H2O))4+29H
(P8W48O184)(NbO(C2O4)(H2O))4+23H+3Li+3NH4
(P8W48O184)(NbO(C2O4)(H2O))4+20H+3Li+6NH4
400
300
200
100
0
-100
-200
-300
-400
1750
1800
1850
1900
m/z

Fig. S8.

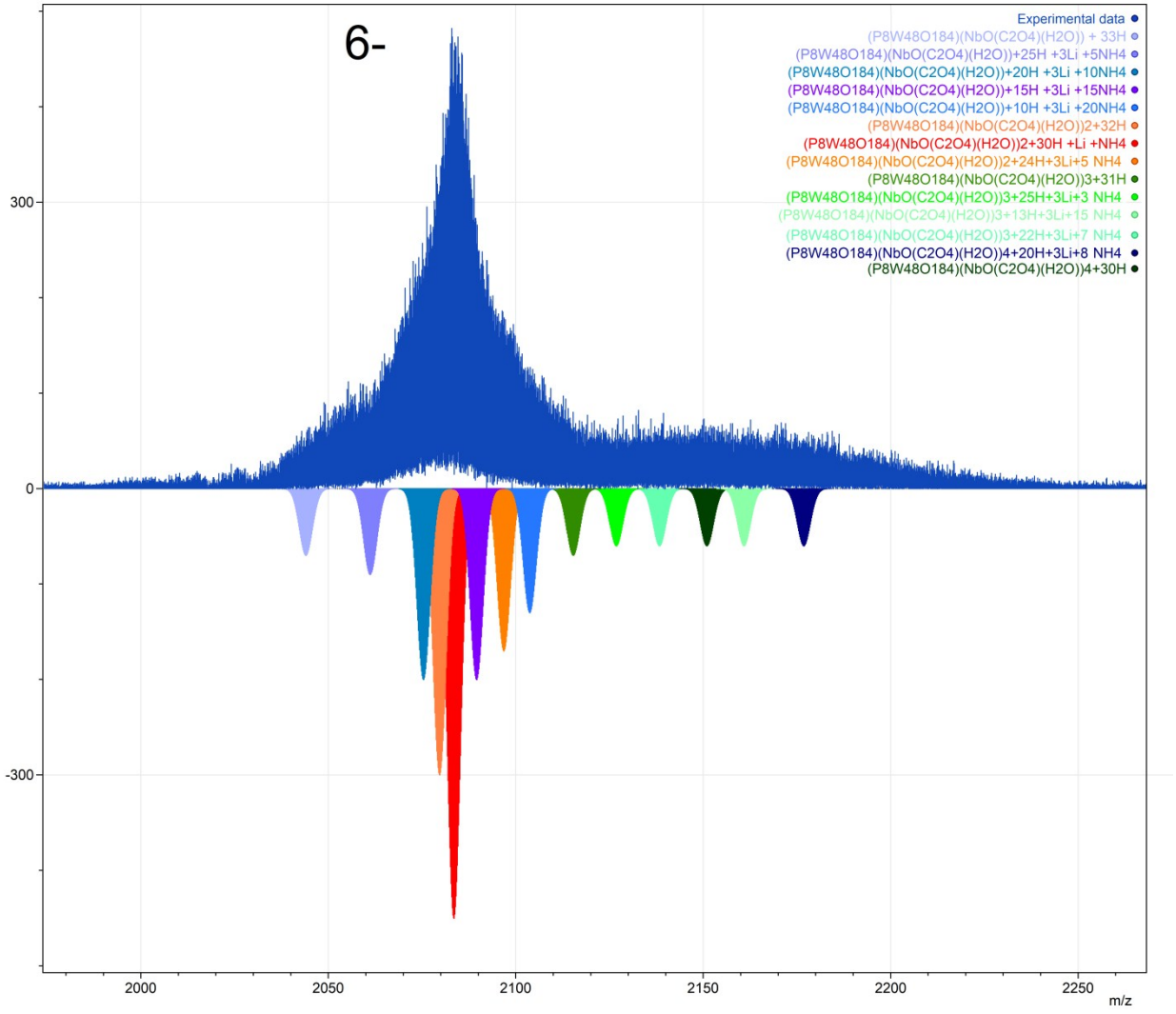

6-
Experimental data
(P8W48O184)(NbO(C2O4)(H2O)) + 33H
(P8W48O184)(NbO(C2O4)(H2O))+25H +3Li +5NH4
(P8W48O184)(NbO(C2O4)(H2O))+20H +3Li +10NH4
(P8W48O184)(NbO(C2O4)(H2O))+15H +3Li +15NH4
(P8W48O184)(NbO(C2O4)(H2O))+10H +3Li +20NH4
(P8W48O184)(NbO(C2O4)(H2O))2+32H
(P8W48O184)(NbO(C2O4)(H2O))2+30H +Li +NH4
(P8W48O184)(NbO(C2O4)(H2O))2+24H+3Li+5 NH4
(P8W48O184)(NbO(C2O4)(H2O))3+31H
(P8W48O184)(NbO(C2O4)(H2O))3+25H+3Li+3 NH4
(P8W48O184)(NbO(C2O4)(H2O))3+13H+3Li+15 NH4
(P8W48O184)(NbO(C2O4)(H2O))3+22H+3Li+7 NH4
(P8W48O184)(NbO(C2O4)(H2O))4+20H+3Li+8 NH4
(P8W48O184)(NbO(C2O4)(H2O))4+30H
300
0
-300
2000
2050
2100
2150
2200
2250
m/z

Fig. S9.

Table S2. Assignment of the ESI-MS spectra.

M/z	Assignment
1362.2	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-}+ 30H^+$
1373.7	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-}+ 22H^+ + 3Li^+ + 5NH_4^+$
1377.5	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-}+ 20H^+ + 3Li^+ + 7NH_4^+$
1381.3	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-}+ 18H^+ + 3Li^+ + 9NH_4^+$
1386.2	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_2^{38-}+ 29H^+$
1395.7	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_2^{38-}+ 23H^+ + 3Li^+ + 4NH_4^+$
1409.9	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_3^{37-}+ 28H^+$
1425.0	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_3^{37-}+ 28H^+ + 3Li^+ + 7NH_4^+$
1439.4	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_4^{36-}+ 22H^+ + 3Li^+ + 2NH_4^+$
1454.5	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_4^{36-}+ 14H^+ + 3Li^+ + 10NH_4^+$
1532.7	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-} + 31H^+$
1535.0	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-} + 28H^+ + 3Li^+$
1541.2	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-} + 25H^+ + 3Li^+ + 3NH_4^+$
1547.9	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-} + 23H^+ + 3Li^+ + 6NH_4^+$
1553.6	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-} + 22H^+ + 2Li^+ + 9NH_4^+$
1559.4	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_2^{38-} + 30H^+$
1561.7	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_2^{38-} + 27H^+ + 3Li^+$
1570.2	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_2^{38-} + 23H^+ + 3Li^+ + 4NH_4^+$
1576.6	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_2^{38-} + 20H^+ + 3Li^+ + 7NH_4^+$
1586.3	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_3^{37-} + 29H^+$
1594.8	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_3^{37-} + 23H^+ + 3Li^+ + 3NH_4^+$
1603.3	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_3^{37-} + 19H^+ + 3Li^+ + 7NH_4^+$
1612.9	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_4^{36-} + 28H^+$
1621.5	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_4^{36-} + 22H^+ + 3Li^+ + 3NH_4^+$
1634.4	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_4^{36-} + 15H^+ + 3Li^+ + 10NH_4^+$
1751.0	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-}+ 32H^+$
1764.1	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-}+ 25H^+ + 3Li^+ + 4NH_4^+$
1769.0	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-}+ 23H^+ + 3Li^+ + 6NH_4^+$
1771.4	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-}+ 22H^+ + 3Li^+ + 7NH_4^+$
1773.8	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-}+ 21H^+ + 3Li^+ + 8NH_4^+$
1776.3	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-}+ 20H^+ + 3Li^+ + 9NH_4^+$
1782.5	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_2^{38-} + 31H^+$
1784.1	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_2^{38-} + 29H^+ + 2Li^+$
1787.4	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_2^{38-} + 27H^+ + 3Li^+ + NH_4^+$
1792.2	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_2^{38-} + 25H^+ + 3Li^+ + 3NH_4^+$
1797.1	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_2^{38-} + 23H^+ + 3Li^+ + 5NH_4^+$
1802.0	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_2^{38-} + 21H^+ + 3Li^+ + 7NH_4^+$
1813.1	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_3^{37-} + 30H^+$
1820.4	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_3^{37-} + 25H^+ + 3Li^+ + 2NH_4^+$
1825.2	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_3^{37-} + 23H^+ + 3Li^+ + 4NH_4^+$
1830.0	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_3^{37-} + 21H^+ + 3Li^+ + 6NH_4^+$
1843.6	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_4^{36-}+ 29H^+$
1853.3	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_4^{36-}+ 23H^+ + 3Li^+ + 3NH_4^+$

1860.7	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_4^{36-} + 20H^+ + 3Li^+ + 6NH_4^+$
2044.1	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-} + 33H^+$
2075.3	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-} + 20H^+ + 3Li^+ + 10NH_4^+$
2079.8	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_2^{38-} + 32H^+$
2083.6	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_2^{38-} + 30H^+ + Li^+ + NH_4^+$
2089.5	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-} + 15H^+ + 3Li^+ + 15NH_4^+$
2096.8	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_2^{38-} + 24H^+ + 3Li^+ + 5NH_4^+$
2103.7	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-} + 10H^+ + 3Li^+ + 20NH_4^+$
2115.4	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_3^{37-} + 31H^+$
2126.8	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_3^{37-} + 25H^+ + 3Li^+ + 3NH_4^+$
2138.4	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_3^{37-} + 22H^+ + 3Li^+ + 7NH_4^+$
2151.0	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_4^{36-} + 30H^+$
2161.0	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_3^{37-} + 13H^+ + 3Li^+ + 15NH_4^+$
2161.1	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))^{39-} + 25H^+ + 3Li^+ + 5NH_4^+$
2176.9	$(P_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_4^{36-} + 20H^+ + 3Li^+ + 8NH_4^+$

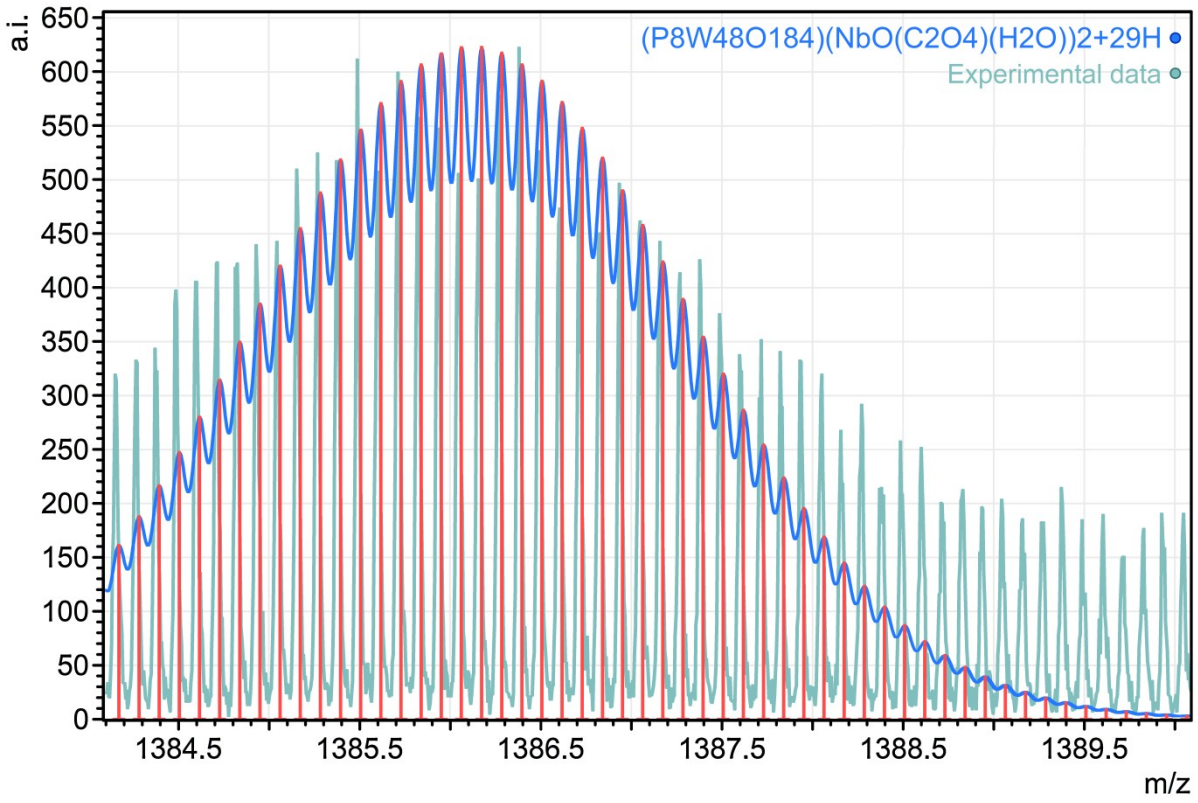


Fig. S10. Comparison between experimental and calculated values of isotopic patterns for $\{[P_8W_{48}O_{184}(NbO(C_2O_4)(H_2O))_2 + 29H^+]^{9-}$

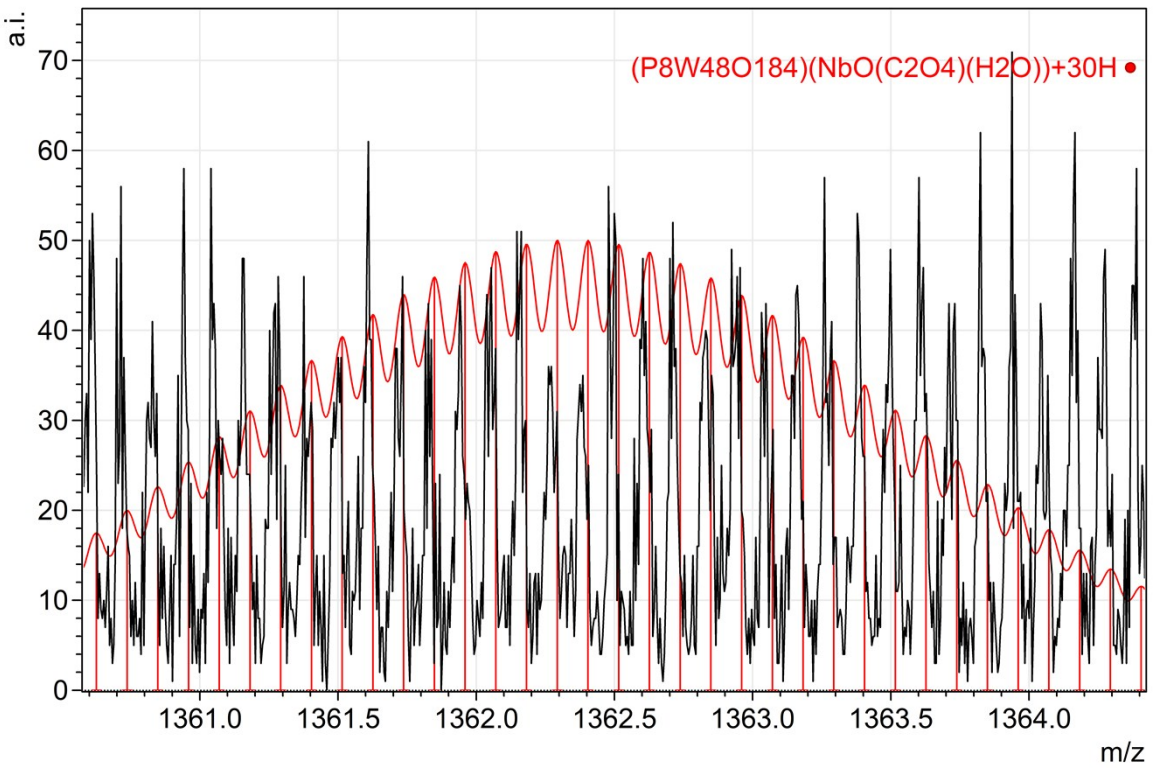


Fig. S11. Comparison between experimental and calculated values of isotopic patterns for $\{[P_8W_{48}O_{184}(NbO(C_2O_4)(H_2O)) + 30H^+]^{9-}$

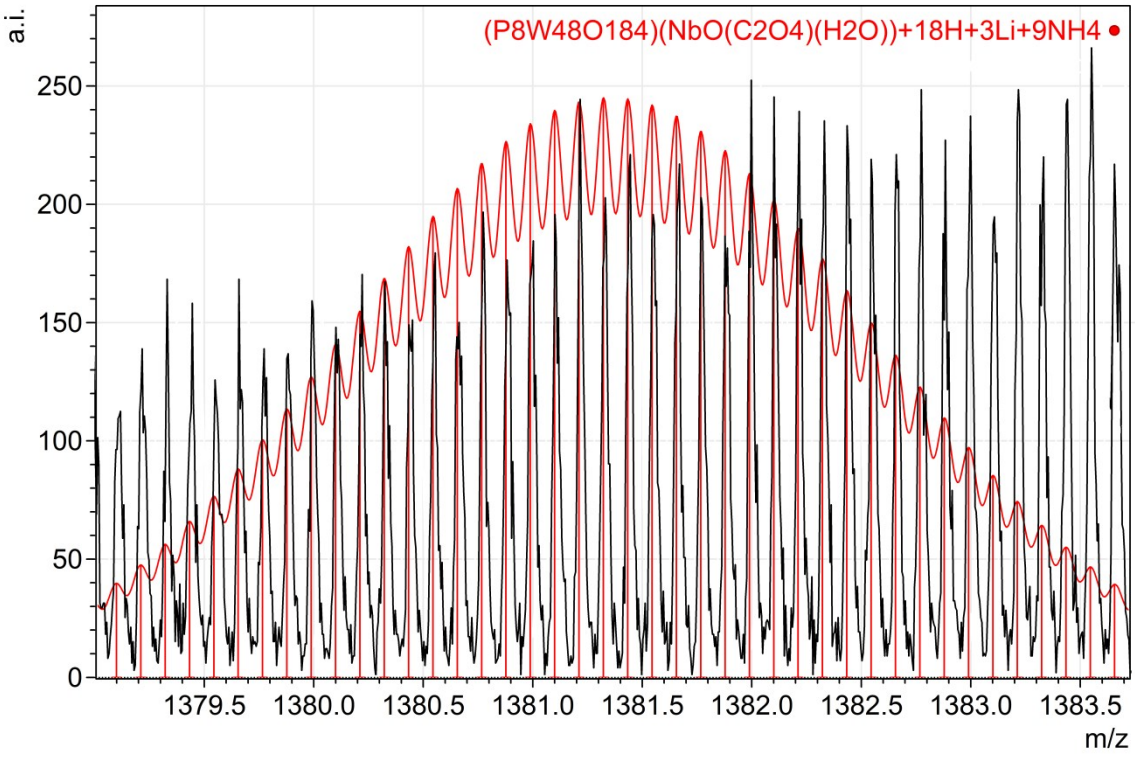


Fig. S12. Comparison between experimental and calculated values of isotopic patterns for $\{[P_8W_{48}O_{184}(NbO(C_2O_4)(H_2O)) + 18H^+ + 3Li^+ + 9NH_4^+]^{9-}$

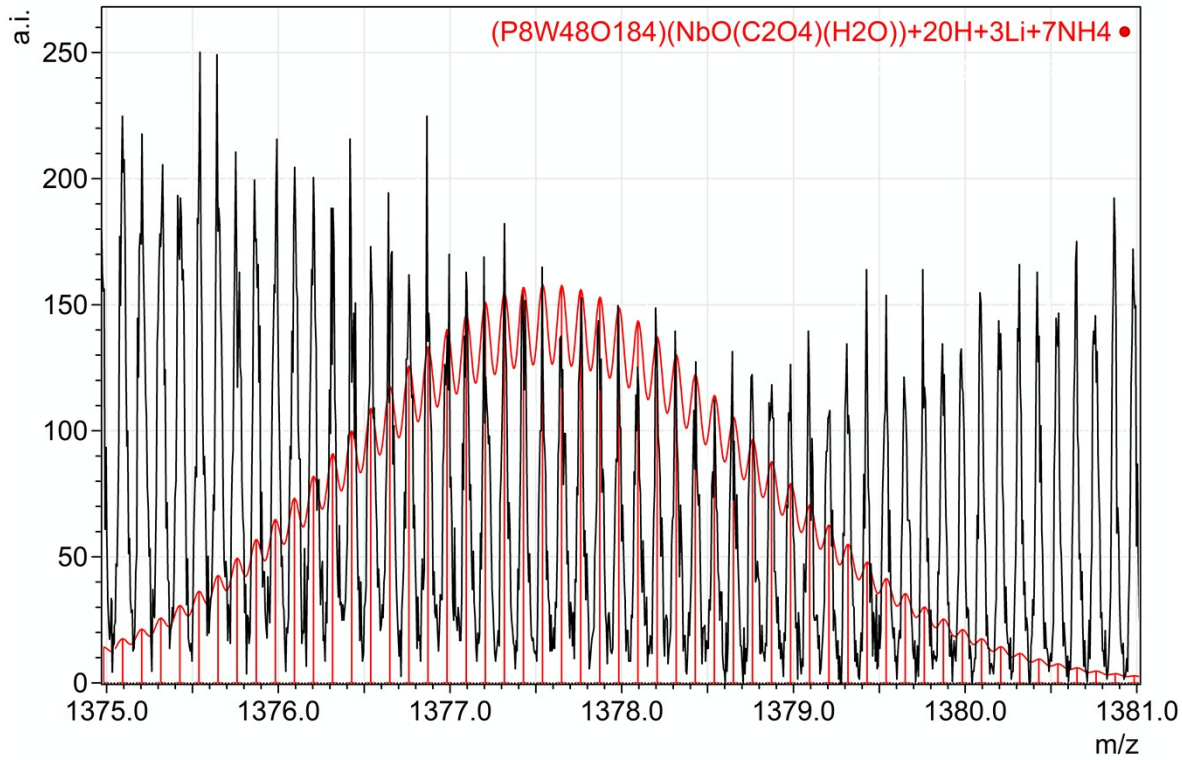


Fig. S13. Comparison between experimental and calculated values of isotopic patterns for $\{[P_8W_{48}O_{184}(NbO(C_2O_4)(H_2O)) + 20H^+ + 3Li^+ + 7NH_4^+]^{9-}$

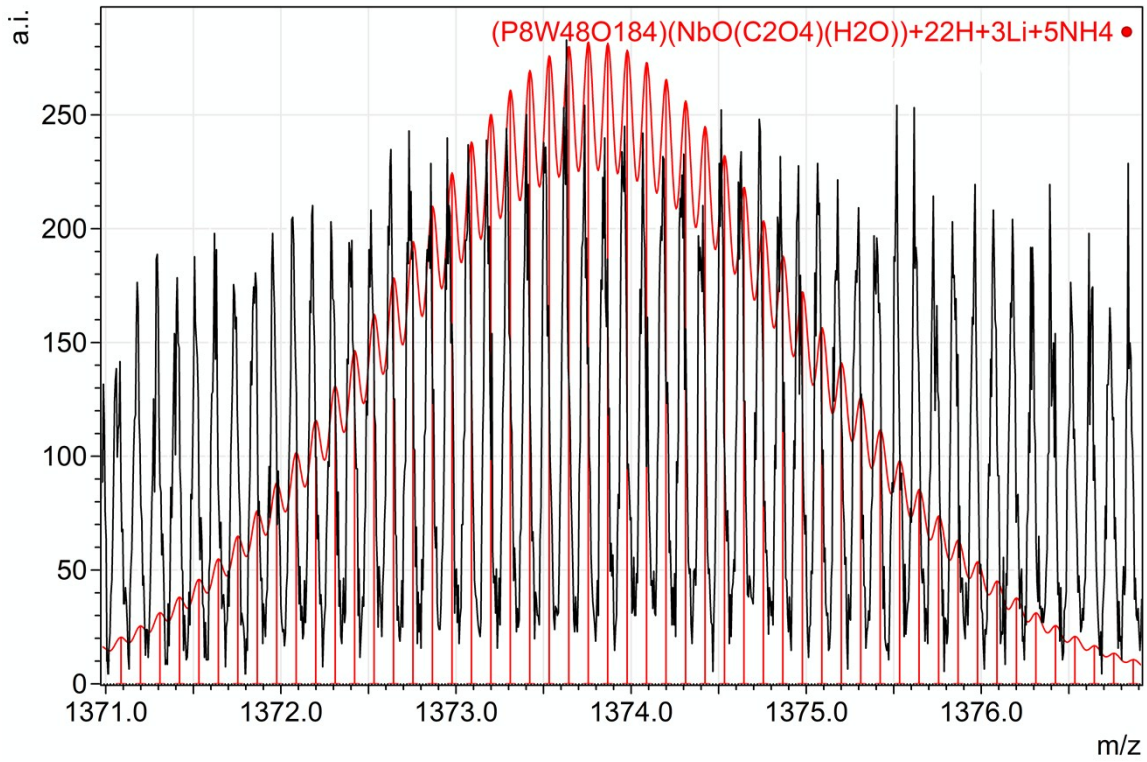


Fig. S14. Comparison between experimental and calculated values of isotopic patterns for $\{[P_8W_{48}O_{184}(NbO(C_2O_4)(H_2O)) + 22H^+ + 3Li^+ + 5NH_4^+]^{9-}$

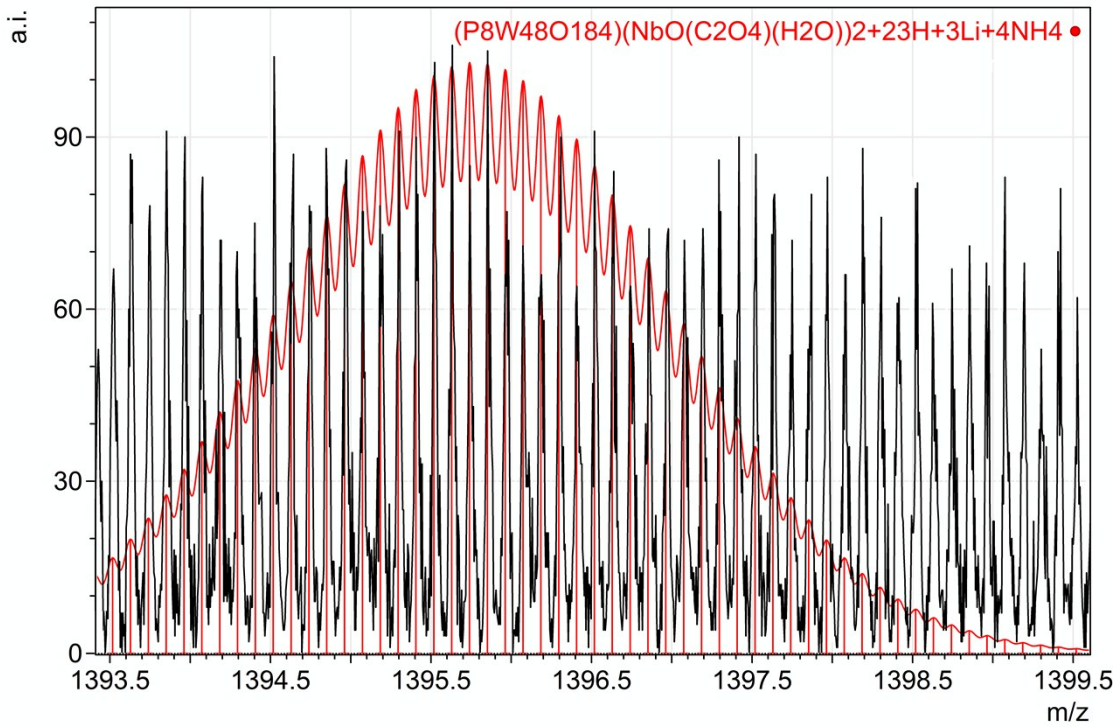


Fig. S15. Comparison between experimental and calculated values of isotopic patterns for $\{[P_8W_{48}O_{184}(NbO(C_2O_4)(H_2O))_2 + 23H^+ + 3Li^+ + 4NH_4^+]^{8-}$

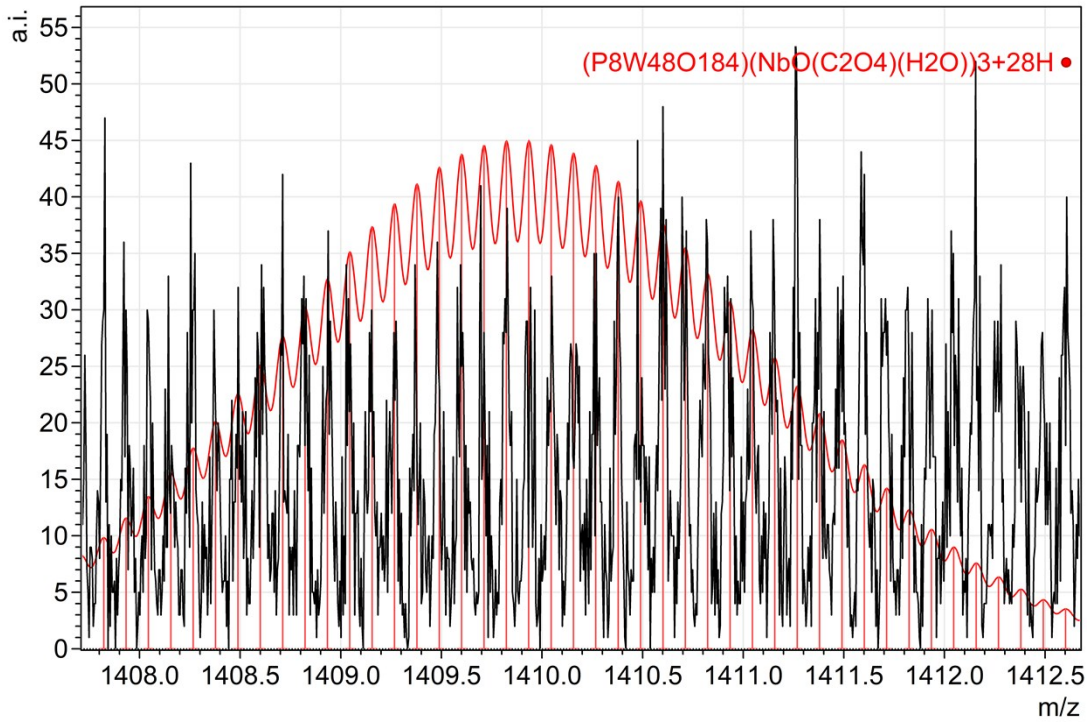


Fig. S16. Comparison between experimental and calculated values of isotopic patterns for $\{[P_8W_{48}O_{184}(NbO(C_2O_4)(H_2O))_3 + 28H^+]^{9-}$

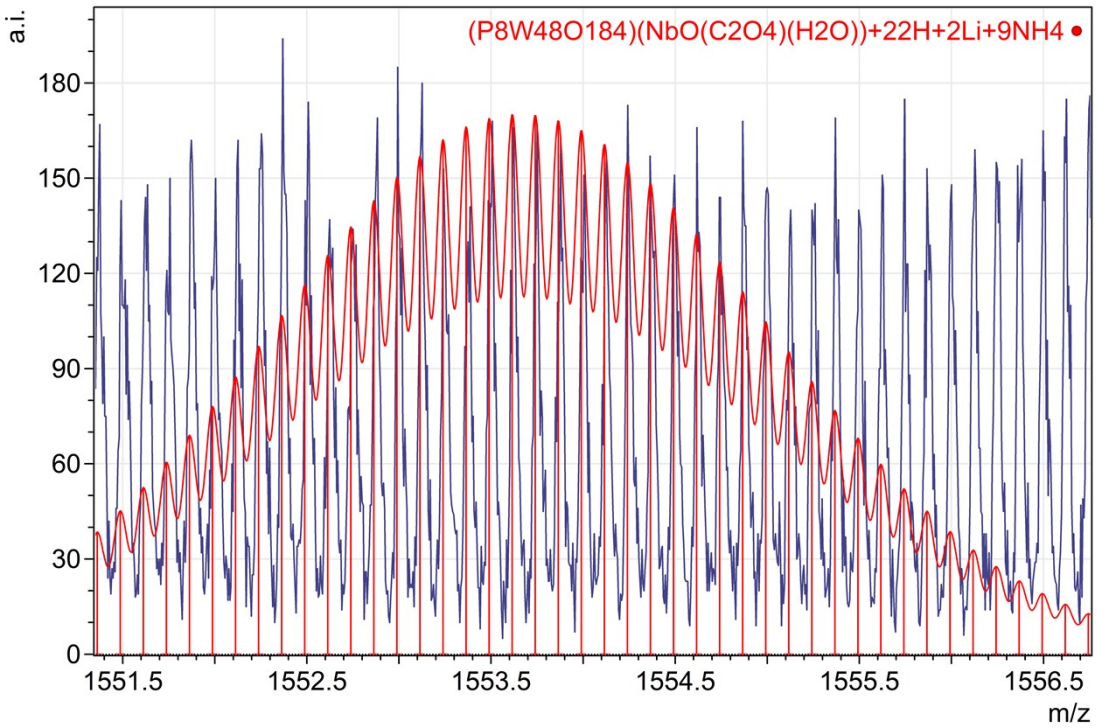


Fig. S17. Comparison between experimental and calculated values of isotopic patterns for $\{[P_8W_{48}O_{184}(NbO(C_2O_4)(H_2O)) + 22H^+ + 2Li^+ + 9NH_4^+]^{6-}$

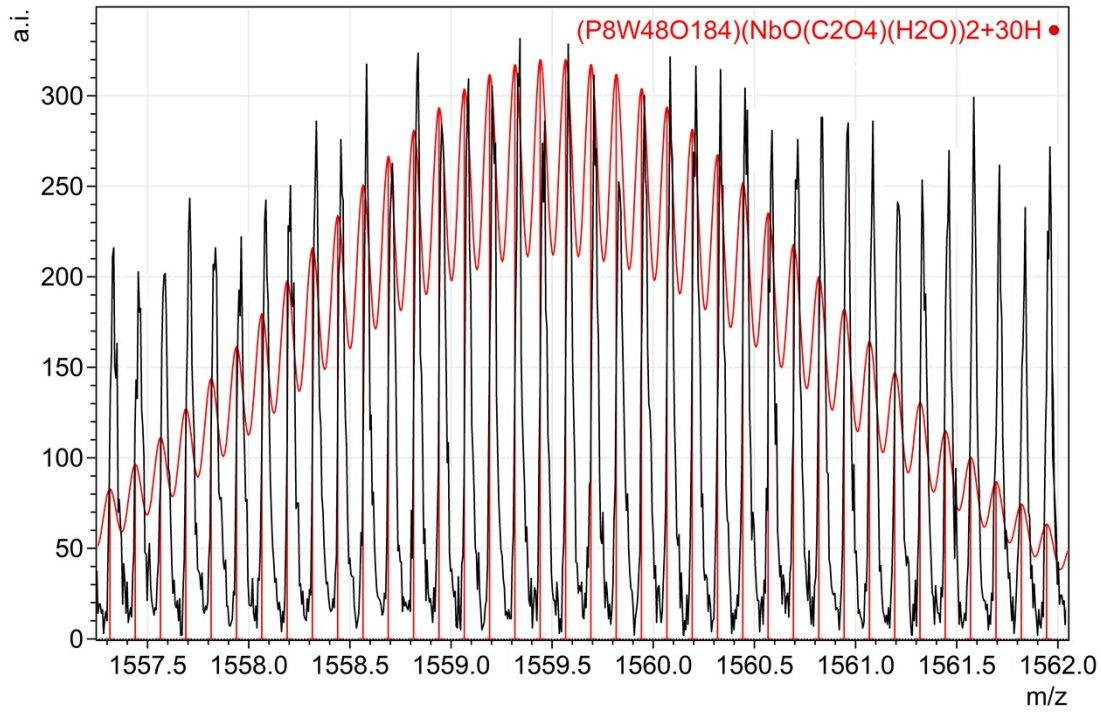


Fig. S18. Comparison between experimental and calculated values of isotopic patterns for $\{[P_8W_{48}O_{184}(NbO(C_2O_4)(H_2O))_2 + 30H^+]^{8-}$

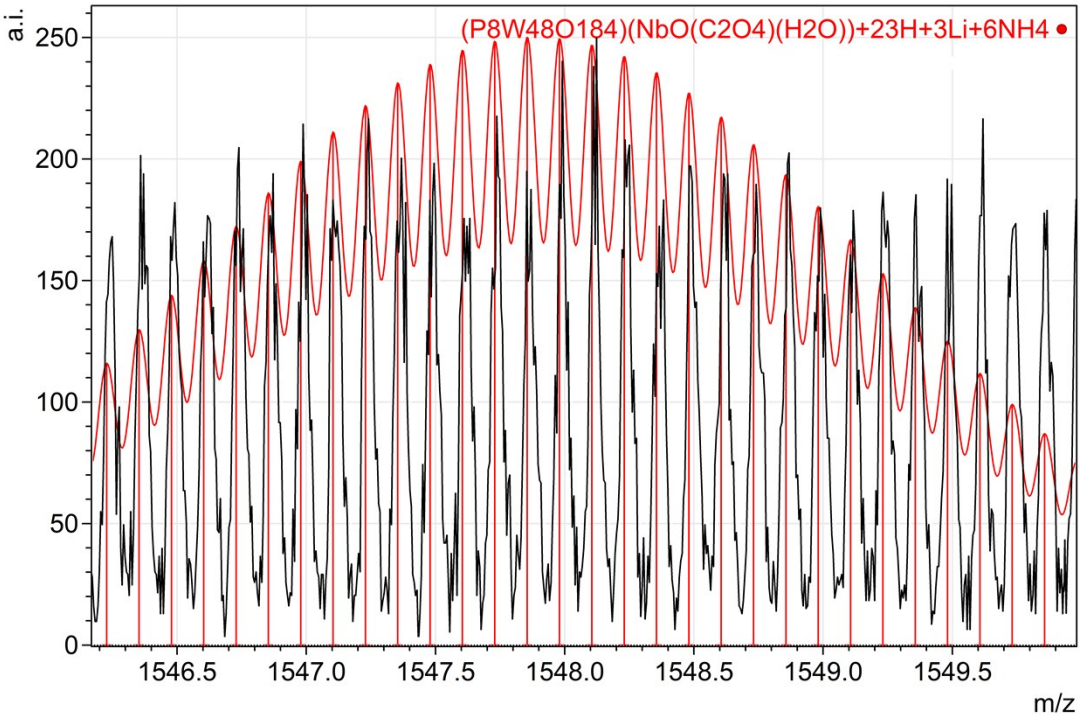


Fig. S19. Comparison between experimental and calculated values of isotopic patterns for $\{[P_8W_{48}O_{184}(NbO(C_2O_4)(H_2O)) + 23H^+ + 3Li^+ + 6NH_4^+]^{7-}$

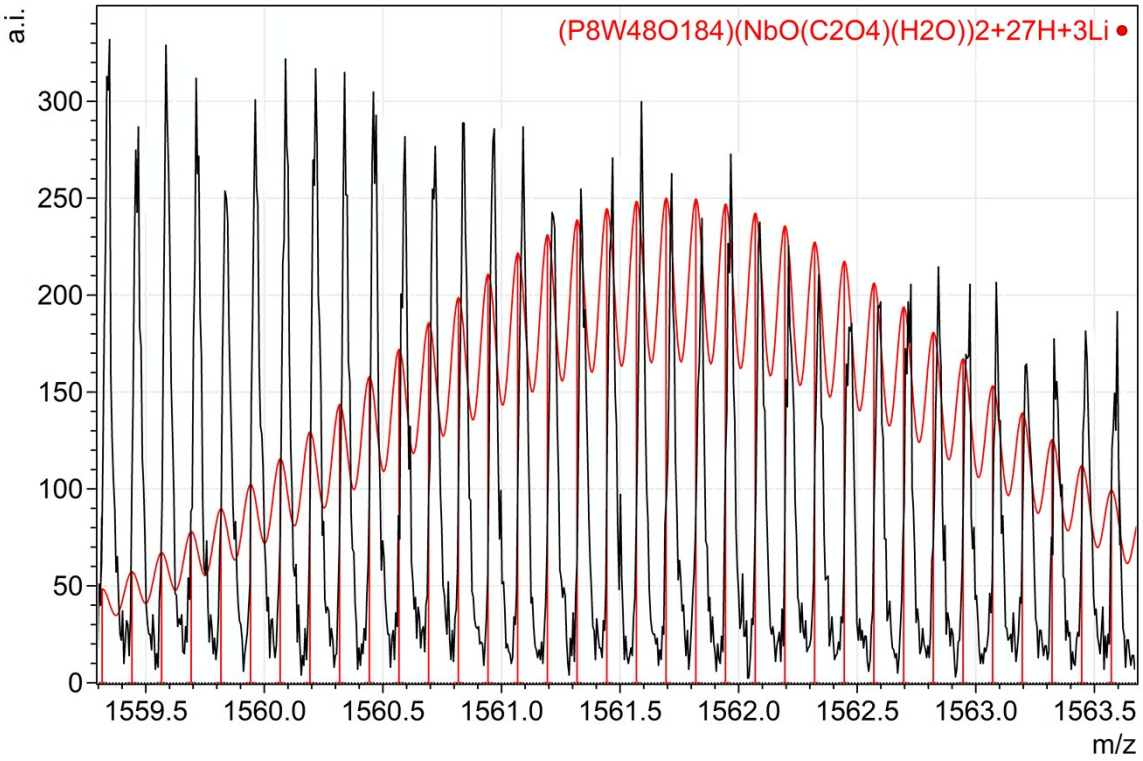


Fig. S20. Comparison between experimental and calculated values of isotopic patterns for $\{[P_8W_{48}O_{184}(NbO(C_2O_4)(H_2O))_2 + 27H^+ + 3Li^+]^{8-}$

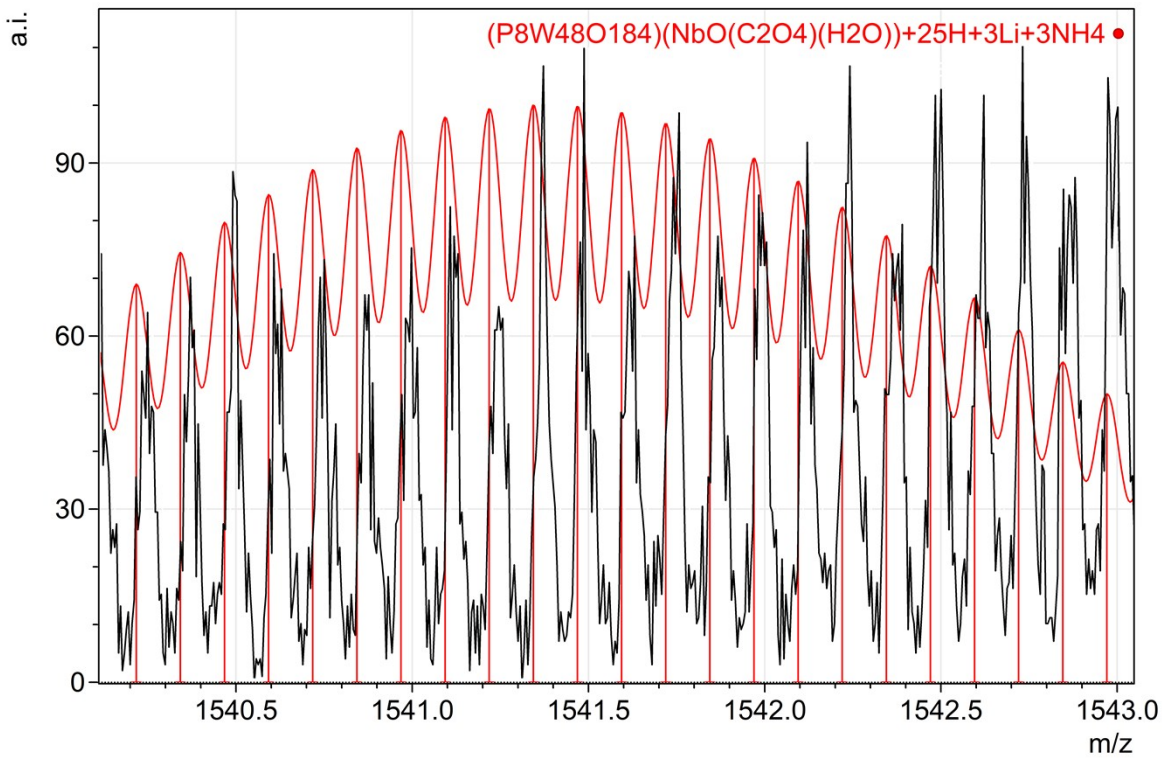


Fig. S21. Comparison between experimental and calculated values of isotopic patterns for $\{[P_8W_{48}O_{184}(NbO(C_2O_4)(H_2O)) + 25H^+ + 3Li^+ + 3NH_4^+]^{8-}$

Table S3. Experimental details

	1
Chemical formula	$Nb_{3.68}O_{238}P_8W_{48}$
M_r	13222.47
Crystal system, space group	Tetragonal, *I*4/*m*
Temperature (K)	130
a, *c* (Å)	25.6122 (5), 22.0939 (5)
V (Å^3)	14493.3 (7)
Z	2
Radiation type	Mo *K*a
μ (mm^{-1})	19.24
Crystal size (mm)	0.12 × 0.08 × 0.05
Diffractometer	New Xcalibur, AtlasS2
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.529, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19190, 6795, 4745
R_{int}	0.036
θ values (°)	θ_{max} = 25.4, θ_{min} = 3.4
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.602
Range of *h*, *k*, *l*	$-28 \le h \le 30$, $-30 \le k \le 29$, $-26 \le l \le 21$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.045, 0.116, 1.02
No. of reflections, parameters, restraints	6795, 386, 0
H-atom treatment	H-atom parameters not defined
Weighting scheme	$w = 1/[s^2(F_o^2) + (0.0458P)^2 + 505.568P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.46, -1.51

Computer programs: *CrysAlis PRO* 1.171.38.41 (Rigaku OD, 2015), *SHELXS2014* (Sheldrick, 2014), *SHELXL2014* (Sheldrick, 2014), ShelXle (Hübschle, 2011), CIFTAB-2014 (Sheldrick, 2014).

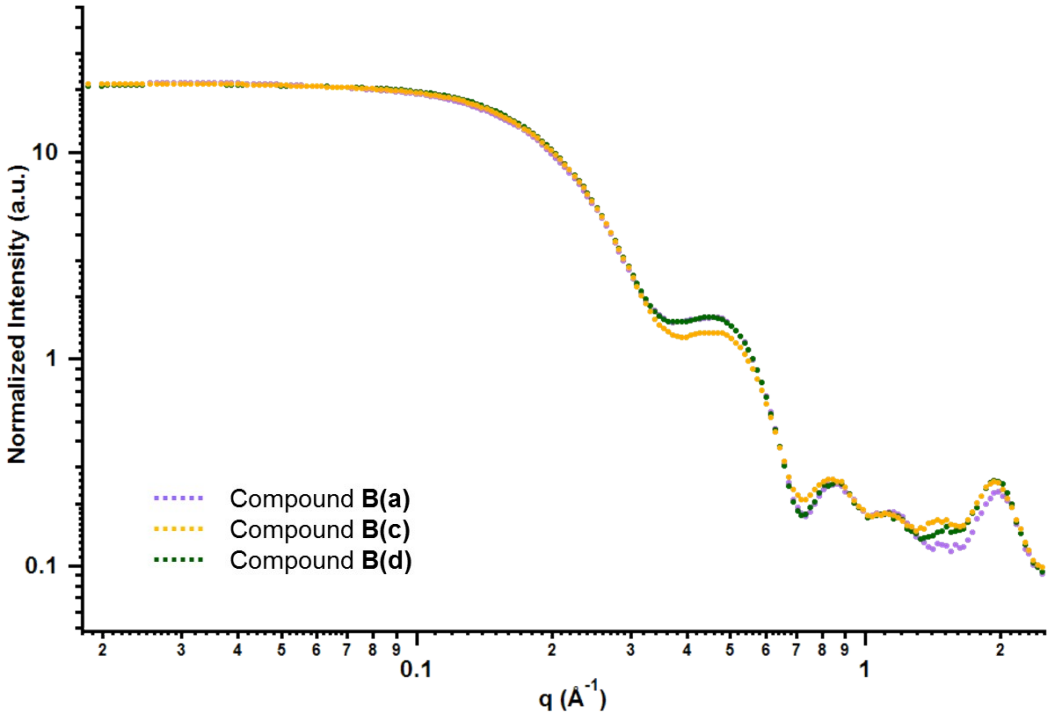


Fig S22. Experimental SAXS curves of the compounds B(a) (purple), B(c) (gold) and B(d) (green).

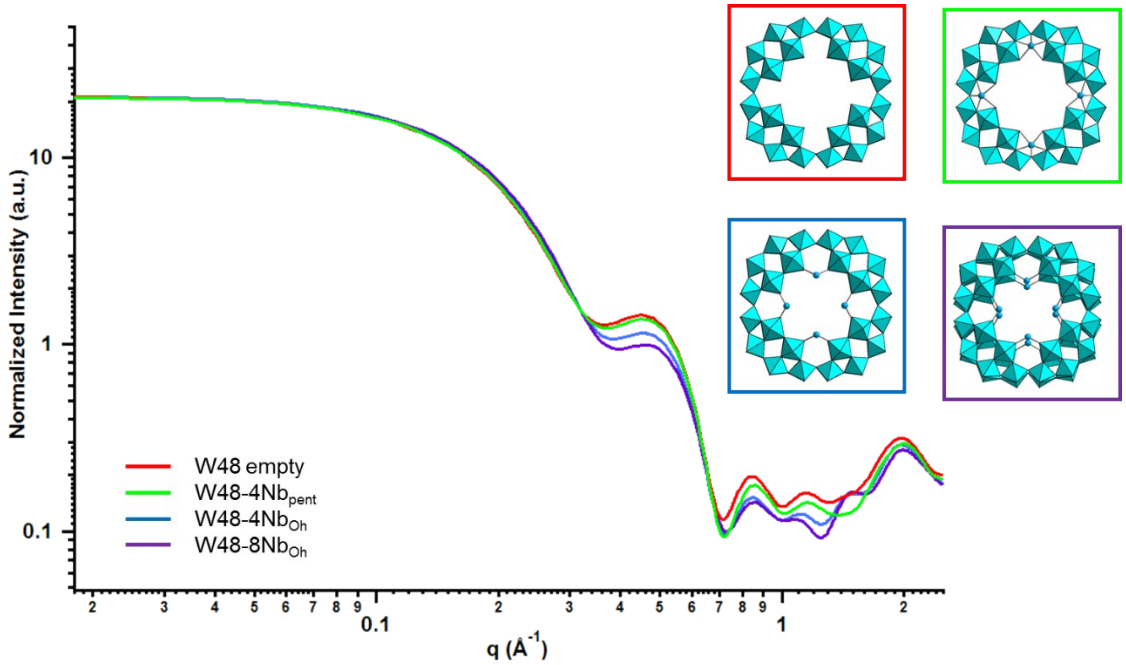


Fig S23. Simulated scattering curves of empty P_8W_{48} cluster (red), P_8W_{48} incorporating 4 Nb in the pentagonal position (green), P_8W_{48} incorporating 4 Nb in the common site-(blue) or P_8W_{48} incorporating 8 Nb in the common site-(purple).

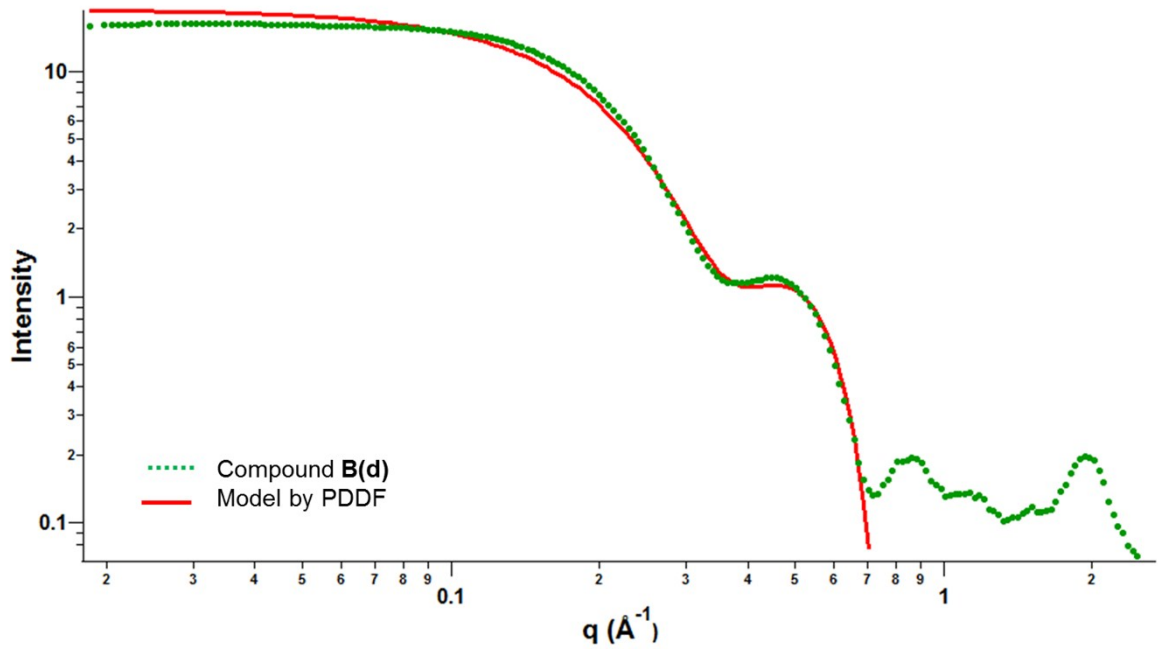


Fig S24. Scattering curve of compound B(d) (green dots) and the calculated scattering curve obtained by PDDF (red).

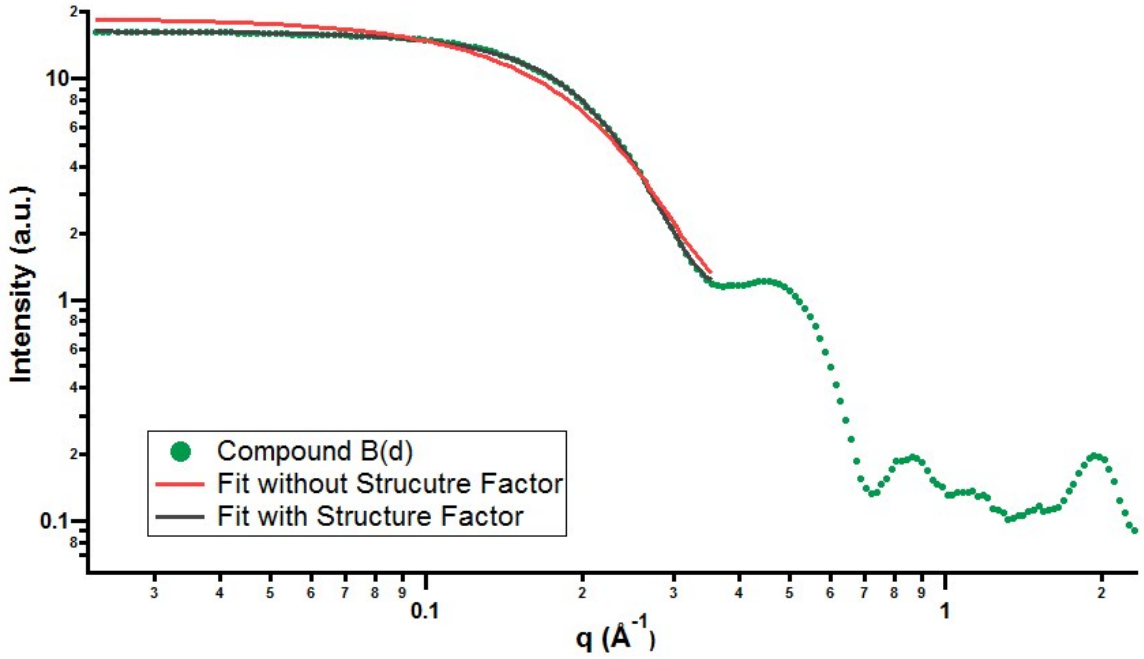


Fig S25. Experimental **s**cattering curve of compound **B(d)** (green dots) along the spherical model fit in a dilute system (red line) and the spherical model including a structure factor : center-to-center distance between clusters = 24.8 Å, and number of nearest neighbors to a cluster = 0.47 (black line).

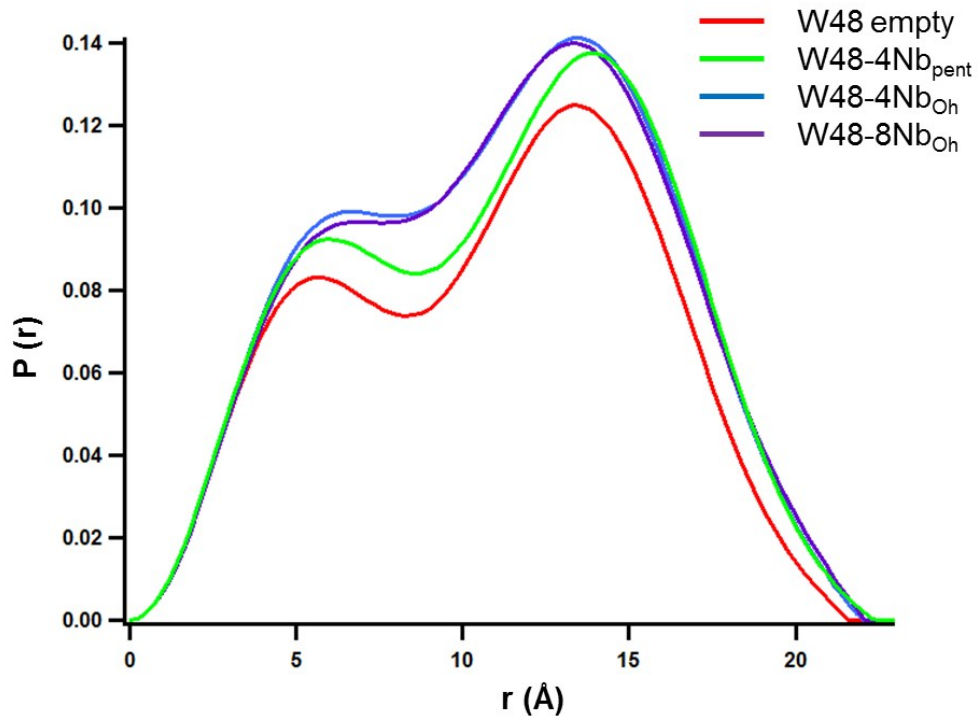


Fig S26. The PDDFs (pair distance distribution function) for empty P_8W_{48} cluster (red), P_8W_{48} incorporating 4 Nb in the pentagonal position (green), P_8W_{48} incorporating 4 Nb in the common site (blue) or P_8W_{48} incorporating 8 Nb in the common site (purple).

Table S4. Size of species determine by PDDF analysis of the scattering curves.

Compound	R_g (Guinier) Å	Diameter (Å)
B(a)	8.41	22.53
B(c)	8.36	22.48
B(d)	8.34	22.00
1*		23.1

* Diameter obtained from the X-ray structure