[Supporting Information]

A novel peroxopolyoxoniobate incorporating mixed heteroatoms: $[P_2Se_2Nb_6(O_2)_6O_{22}]^{8-}$

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CONTENTS

Section 1 Experimental Section

1.1 Materials and Methods

$K_7HNb_6O_{19}\cdot 13H_2O$ was synthesized according to the literature and successfully characterized by IR spectrum.[S1]The other chemicals were used as obtained without additional purification. The IR spectra were recorded by using a Bruker VERTEX 70 FT-IR spectrometer in the range of 4000–400 cm^{-1}(used KBr for solid sample palletized). XPRD data were performed on a Bruker AXS D8 Advance diffractometer with Cu Kα radiation in the 2θ = 5-45° range at 293 K. TGA was performed under a N_2 atmosphere by using a Mettler-Toledo TGA/ SDTA851^e instrument with a heating rate of 10 ℃ min^{-1}. Elemental analyses of Cs, P, Se and Nb were performed by using a PerkinEimer Optima 2000 ICP-OES spectrometer. ESI-MS measurements were performed on an AB SCIEX Triple TOF 4600 spectrometer operating in negative ion mode and data was analyzed using the Peakview 2.0 software provided.

1.2 Synthetic

Synyhesis of **1**: $K_7HNb_6O_{19}\cdot 13H_2O$ (2.00 g, 1.47 mmol) was solubilized in 225 ml aqueous H_2O_2 (25 ml of a 30% aqueous solution dissolved in 200 ml of deionized water) with stirring. Then a solution of Na_2SeO_3 (1.38 g, 11.50 mmol) in H_2O (5 ml) and another solution of $NaH_2PO_4\cdot 2H_2O$ (0.62 g, 3.97 mmol) in H_2O (5 ml) were added in turn. Under rapid stirring, 6 M HCl was added dropwise to give a clear, yellow and effervescent solution of pH = 2.20. Finally, the resulting mixture was heated to 90 ℃ for 3h. After this period, the mixture was gradually cooled to room temperature, followed by the addition of 1.5 ml of 6M CsCl. The solution was stirred at room temperature for 20 min, filtered and then was kept in air for slow evaporation at room temperature. After 24 h, the yellow stick-shaped crystals of compound **1** were obtained. Yield: 50% based on $K_7HNb_6O_{19}\cdot 13H_2O$. Analysis (calcd., found for $Cs_4H_4Nb_6O_{44}P_2Se_2$): Cs (26.35, 26.09), P (3.07, 3.04), Se (7.63, 7.75), Nb (27.64, 27.36). IR (KBr-pellet): 1063, 867, 789, 684, 545, 492 cm^{-1}.

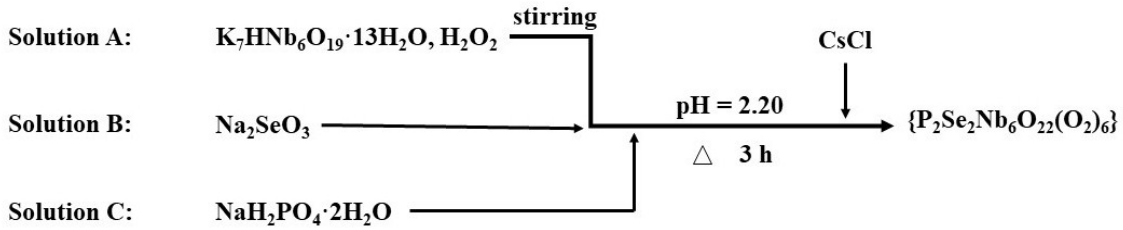


Fig. S1 The experimental process.

1.3 X-ray Crystallography

Table S1 Crystal data and structure refinements for **1**.

	1
empirical formula	$Cs_4H_{24}Nb_6O_{44}P_2Se_2$
M_r	2037.09
T [K]	296.15
crystal system	triclinic
space group	P-1
a [Å]	10.118(2)
b [Å]	10.424(3)
c [Å]	11.089(3)
α [°]	94.043(4)
β [°]	103.437(4)
γ [°]	117.660(4)
V [Å^3]	985.8(4)
Z	1
μ [mm^{-1}]	7.362
F(000)	868
crystal size [mm^3]	0.3 × 0.2 × 0.18
2θ range [°]	3.86 - 50.192
index ranges	$-11 \le h \le 12$ $-11 \le k \le 12$ $-13 \le l \le 13$
reflections collected	4839
independent reflections	3464 [R_{int} = 0.0258, R_{sigma} = 0.0540]
data/restraints/parameters	3464/12/235
goodness-of-fit on F^2	1.066
final R indexes (I>=2σ (I))[a]	R_1 = 0.0731, wR_2 = 0.2004
final R indexes (all data)[b]	R_1 = 0.0926, wR_2 = 0.2177

[a] $R_1 = \sum||F_0| - |F_c||/\sum|F_0|$.

[b] $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]\}^{1/2}$.

Section 2 Supplementary tables and structural figures

Table S2 The BVS calculations of all the Nb, P and Se atoms on polyanion **1**.

Atom lable	Calc. For Nb(V)
Nb(1)	5.27
Nb(2)	5.35
Nb(3)	5.34
Atom lable	Calc. For Se(IV)
Se(1)	4.21
Atom lable	Calc. For Se(V)
P(1)	5.32

Table S3 The bond valence sum calculations of all the oxygen atoms on polyanion **1.**

Atom	Bond valence	Atom	Bond valence
O(1)	1.51	O(10)	1.98
O(2)	1.89	O(11)	1.29
O(3)	1.89	O(12)	2.09
O(4)	1.92	O(13)	1.41
O(5)	1.92	O(14)	1.94
O(6)	1.00	O(15)	2.00
O(7)	2.11	O(16)	1.25
O(8)	1.00	O(17)	1.96
O(9)	1.96		

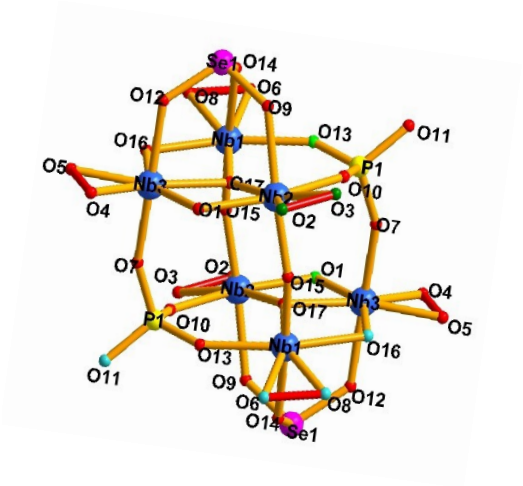


Fig. S2 Charge distribution of O atoms in **1**. Oxygen atoms with different bond valence sums are represented by different colors.

Table S4. The bond valence sum range of all the oxygen atoms on polyanion **1**.

Oxygen	Bond valence sum range	Number	Oxygen	Bond valence sum range	Number
	1.0-1.3	4		1.6-1.9	2
	1.3-1.6	2		1.9-2.2	9

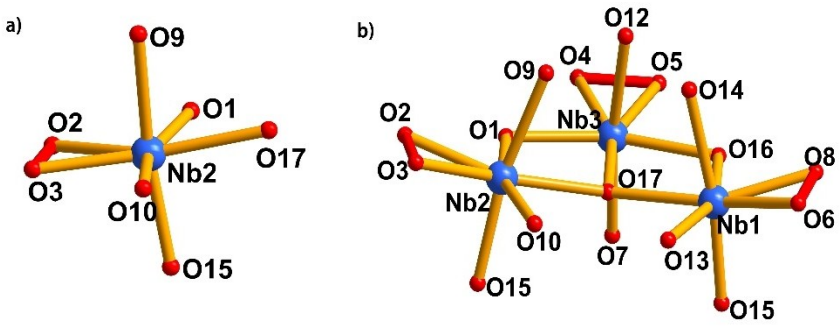


Figure S3. Ball-and-stick representations of the NbO_7 coordination environment (a) and $\{Nb_3(O_2)_3O_{11}\}$ (b).

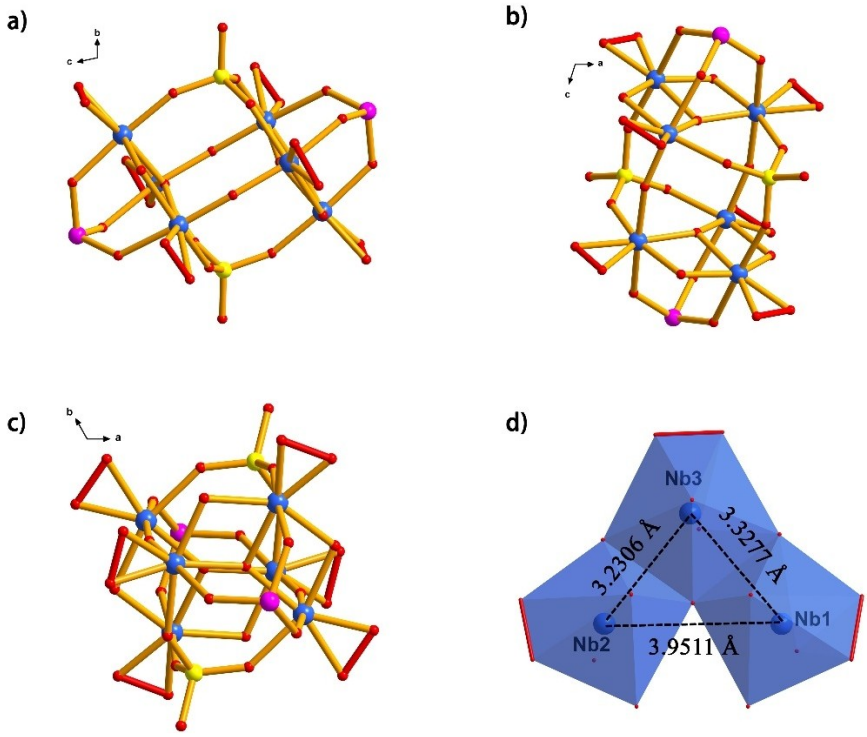


Fig. S4 Viewing from different direction of stick representations of polyanions 1 (a-c). The trinuclear $\{Nb_3(O_2)_3O_{11}\}$ fragment in **1** (d).

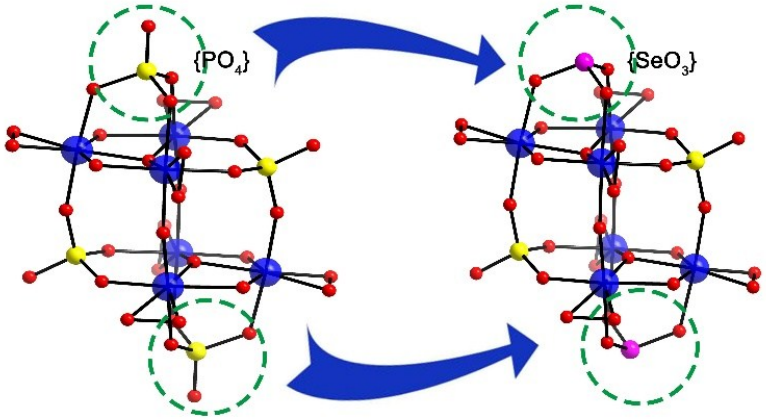


Fig. S5 Ball-and-stick representation of $\{P_2Se_2Nb_6O_{34}\}$ (left) and $\{H_7Nb_6P_4O_{36}\}$ (right) subunits.

Table S5 Charge-density of PONbs and POWs.

POM	Anionic charge	non-hydrogen atoms	Charge density (charge per atom)
$[Nb_6O_{19}]$	8	25	0.32
$[Ti_2Nb_8O_{28}]$	8	38	0.21
$[Nb_{10}O_{28}]$	6	38	0.16
$[SiNb_{12}O_{40}]$	16	53	0.3
$[(PO_2)_3PNb_9O_{34}]$	15	53	0.28
$[H_2Si_4Nb_{16}O_{56}]$	14	76	0.18
$[W_6O_{19}]$	2	25	0.08
$[SiW_{12}O_{40}]$	4	53	0.075
$[SiW_{11}O_{39}]$	8	51	0.16
$[PW_9O_{34}]$	9	44	0.2
Compound **1**	8	44	0.18

Section 3 Additional measurements

3.1 X-ray Powder Diffractograms

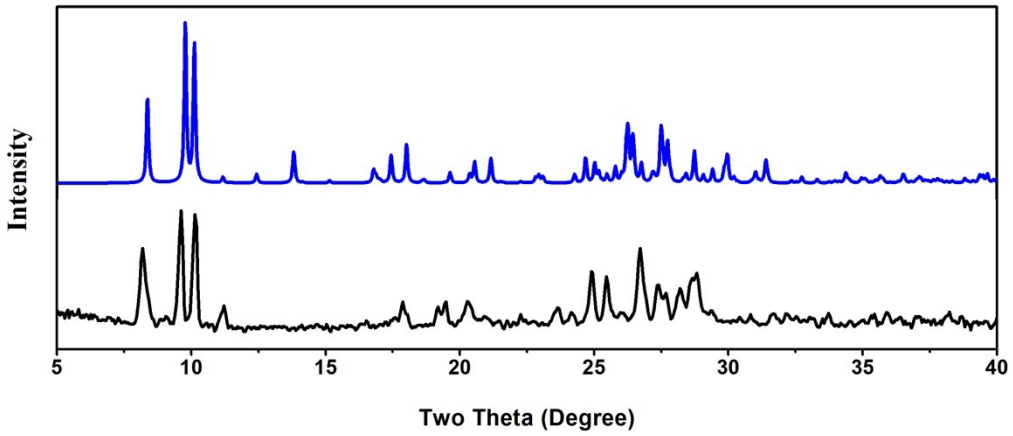


Fig. S6 The PXRD pattern (bottom) of **1** and its calculated pattern (top) based on the single-crystal solution.

The experimental XRPD patterns agree well with the simulated patterns indicating the phase purity in cluster **1**.

3.2 IR Spectra

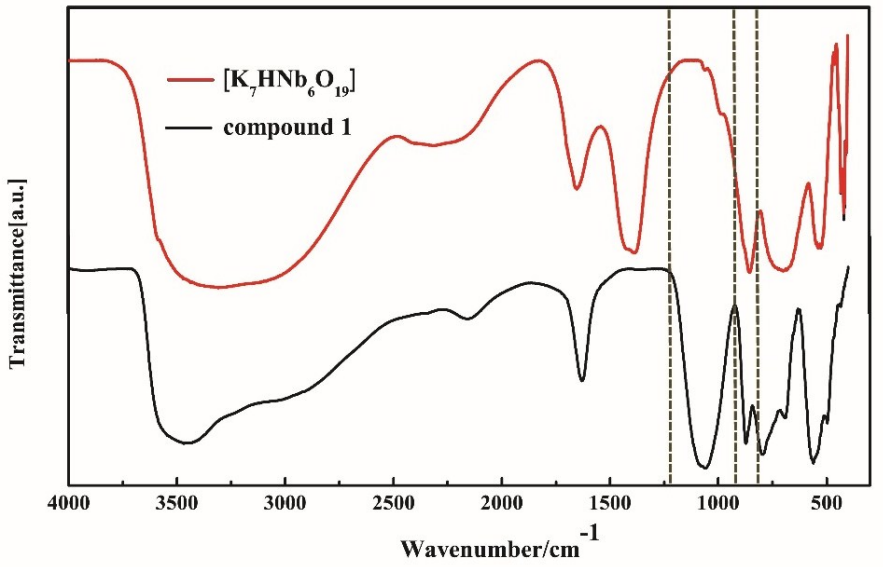


Fig. S7 IR spectra of $K_7HNb_6O_{19}\cdot 13H_2O$ and compound **1**.

3.3 Thermogravimetric analysis

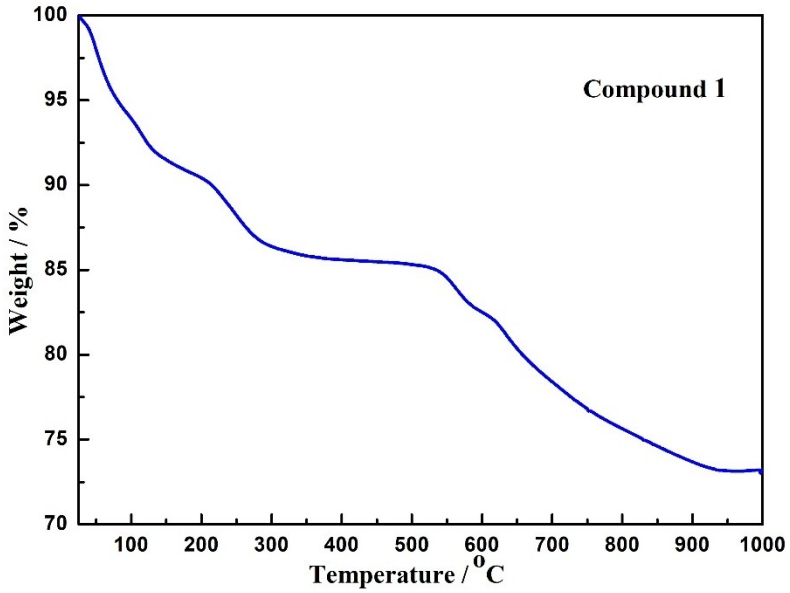


Fig. S8 The TG curves of **1** were measured in the range of 25-1000 ℃ under nitrogen gas atmosphere with the heating rate of 10 ℃/min.

3.4 ESI-MS

These solutions were filtered and introduced to the spectrometer via direct injection at a flow rate of 5 μL min^{-1} using a syringe pump. Spectrometer settings were kept the same throughout and were as follows: ionspray voltage: -4500 V, curtain gas flow, 25 PSI; ion source gas 1, 15 PSI; ion source gas 2, 15 PSI; ion energy 1, -1.1 V; pulse frequency, 11.332 KHz; pulse 1 duration, 3.902 us; declustering potential, -10 V; collision energy, -5.0 V.

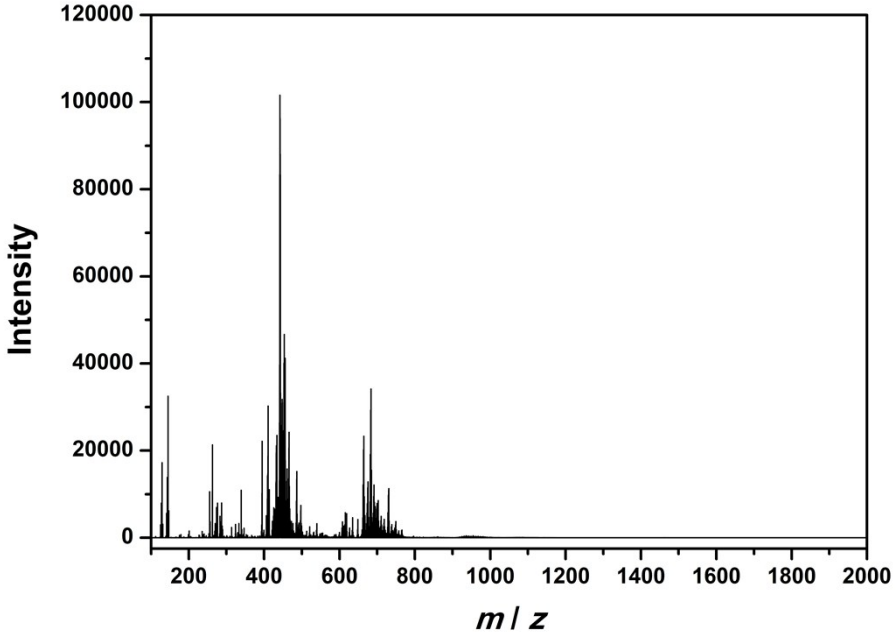
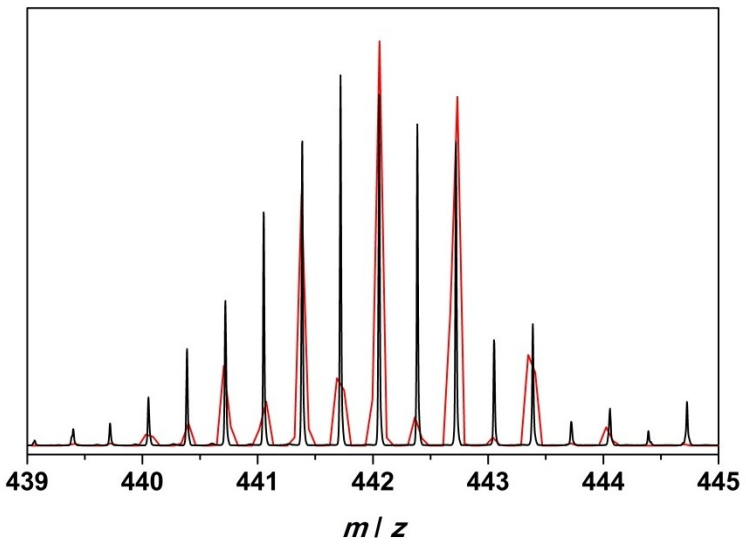


Fig. S9 The ESI-MS of **1** (the overall scale).

Table S6 The assignment of mass spectral data for compound **1**.

m/z (obs.)	peaks Assignment	m/z (calc.)
442.21	$\{H_5P_2Se_2Nb_6O_{34}\}^{3-}$	442.11
447.98	$\{H_5P_2Se_2Nb_6O_{34}(H_2O)\}^{3-}$	448.11
663.62	$\{H_6P_2Se_2Nb_6O_{34}\}^{2-}$	663.67
681.40	$\{H_6P_2Se_2Nb_6O_{34}(H_2O)_2\}^{2-}$	681.68
690.66	$\{H_6P_2Se_2Nb_6O_{34}(H_2O)_3\}^{2-}$	690.69
699.63	$\{H_6P_2Se_2Nb_6O_{34}(H_2O)_4\}^{2-}$	699.70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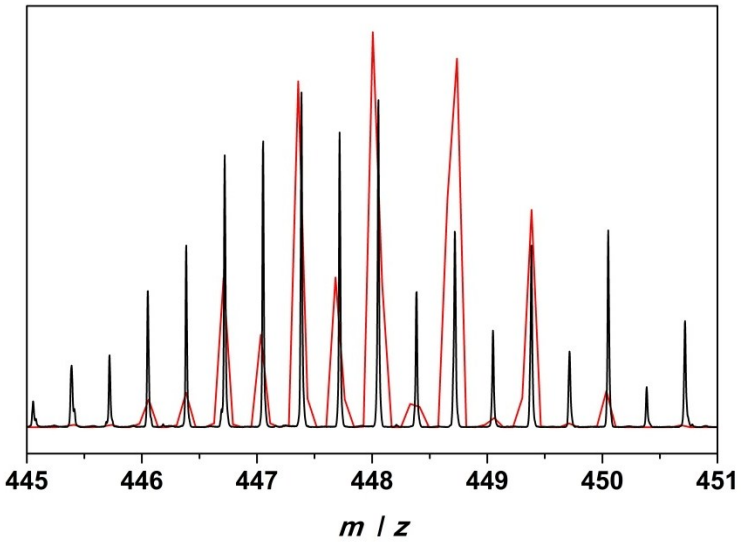
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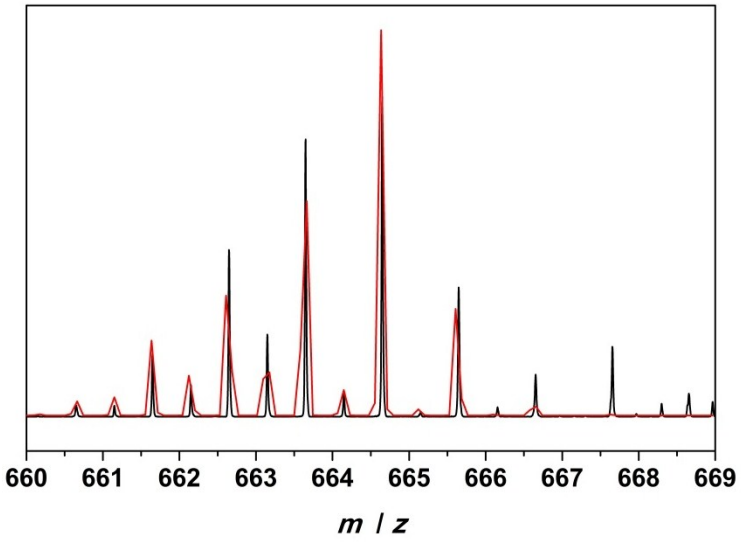
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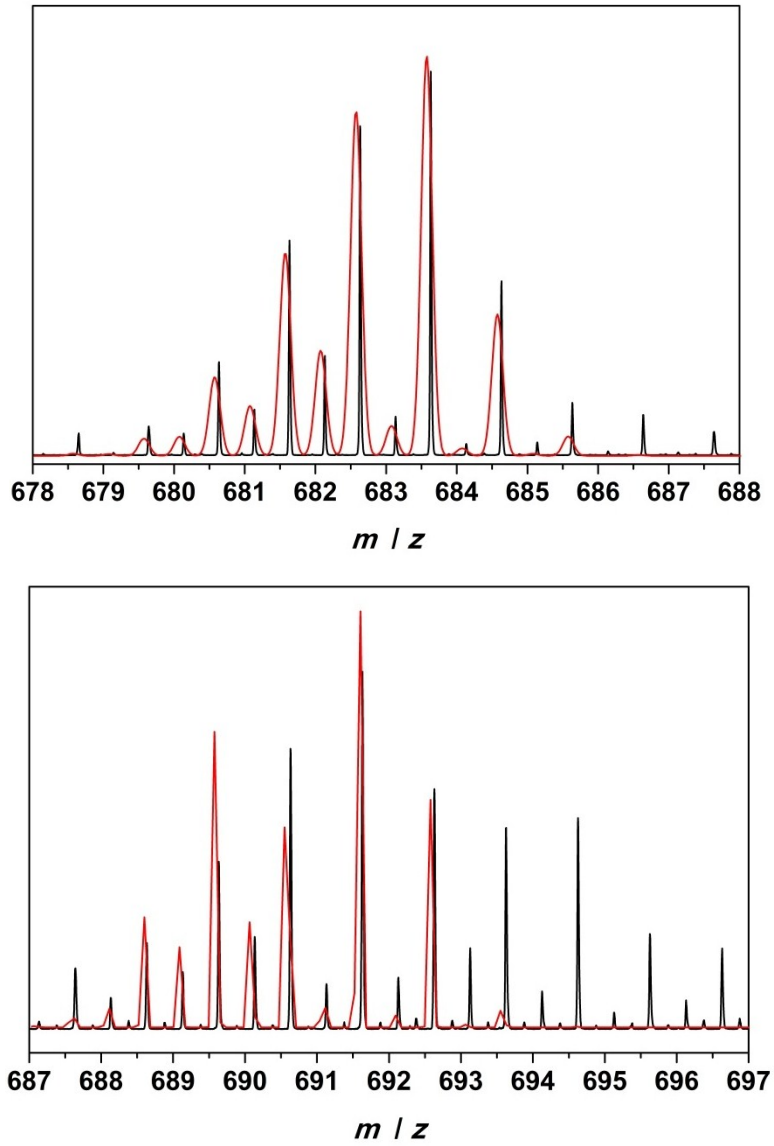

Fig. S10 Simulated (red) and experimental (black) negative-mode mass spectra of isotopic envelopes for compound **1**.

Section 4 References

S1 C. M. Flynn and G. D. Stucky, *Inorg. Chem.*, 1969, **8**, 178.