Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Polyoxometalates with Tunable Third-order Nonlinear Optical and Superbroadband Optical Limiting Properties

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Table S1. Crystal data collection and structure refinement parameters of **V_1Mo_5**, **V_8Mo_2** and **V_9Mo_1**.

	V_1Mo_5	**V_8Mo_2**	**V_9Mo_1**
Empirical formula	$C_{48}H_{108}N_3O_{19}Mo_5V$	$C_{68}H_{150}N_6O_{28}Mo_2V_8$	$C_{68}H_{151}N_6O_{28}MoV_9$
Formula weight	1562.015	2099.34	2055.34
Crystal description	yellow, block	yellow, block	orange, block
Temperature(K)	298(2)	150(2)	150(2)
Wavelength(Å)	0.71073	0.71073	0.71073
Cryst. syst.	Monoclinic	Triclinic	Triclinic
Space group	C2/c	P-1	P-1
a(Å)	30.146(6)	16.747(3)	16.748(3)
b(Å)	18.397(4)	17.427(4)	17.445(4)
c(Å)	27.281(6)	17.929(4)	17.931(4)
α(°)	90	74.18(3)	74.20(3)
β(°)	72.366(3)	67.43(3)	67.40(3)
γ(°)	90	74.13(3)	74.19(3)
V(Å3)	13987(5)	4564.1(17)	4570.1(17)
Z	4	2	2
ρ_{calc}/g·cm-3	1.484	1.528	1.493
2θ range /deg	0.993 - 27.48	0.978 - 25.40	1.34 - 26.37
μ(mm−1)	1.058	1.118	1.081
F(000)	6416	2184	2146
Reflns. collec.	62931	44966	45574
Data/Parameters	15897/694	16444/1106	18623/1016
R(int)	0.0310	0.0640	0.0450
R^a/Rw^b	0.0430/ 0.1449	0.0720/0.2114	0.0728/ 0.1893
GOF (F_2)	1.075	1.023	1.081
CCDC NO.	2080750	2080751	2080752

Table S2. Selected bond lengths and bond angles of **V_1Mo_5**, **V_8Mo_2** and **V_9Mo_1**.

	V_1Mo_5	$(TBA)_2[Mo_6O_{19}]$
M=O(Å)	1.664(3) ~ 1.683(3)	1.674(3) ~ 1.680(3)
M─μ_2-O(Å)	1.875(2) ~ 1.957(3)	1.904(3) ~ 1.942(3)
M─μ_6-O(Å)	2.296(2) ~ 2.3088(5)	2.307(2) ~ 2.326(2)
M···M(Å)	3.239 ~ 3.274	3.269 ~ 3.285

	V_8Mo_2	**V_9Mo_1**	$(TBA)_3[H_3V_{10}O_{28}]$
V=O(Å)	1.596(3) ~1.603(3)	1.591(3) ~ 1.601(4)	1.595(6) ~1.623(4)
M=O(Å)	1.606(4) ~1.615(4)	1.607(4) ~ 1.625(4)	_
M─μ_2-O(Å)	1.803(3) ~1.897(3)	1.804(3) ~ 2.000(3)	1.814(3) ~ 2.030(2)
M─μ_3-O(Å)	1.682(3) ~ 1.689(3)	1.680(3) ~ 1.691(3)	1.939(9) ~2.098(5)
M─μ_3-O(Å)	1.921(3) ~ 2.024(3)	2.023(3) ~ 2.054(3)	_
M─μ_6-O(Å)	2.089(3) ~2.339(3)	2.093(3) ~ 2.341(3)	2.064(1) ~2.349(3)
M···M(Å)	3.0642(12)~3.1989(11)	3.0627(11)~3.1557(17)	3.072(5)~3.247(9)

Table S3. BVS results of V_1Mo_5.

Compound	V_1Mo_5						
	VMo1	VMo2	VMo3		VMo4	VMo5	VMo6
O(1)	1.87			**O(11)**	1.92		
O(2)		1.9		**O(12)**		1.83	
O(3)			1.99	**O(13)**			1.88
O(4)	0.86	0.81		**O(14)**	0.81	0.94	
O(5)	0.93		0.78	**O(15)**	0.84		0.91
O(6)	0.82		0.93	**O(16)**	0.91	0.86	
O(7)	0.80	0.94		**O(17)**	0.93		0.8
O(8)		0.77	0.97	**O(18)**		0.84	
O(9)		0.99	0.77	**O(19)**		0.86	0.88
O(10)	0.29	0.29	0.30	**O(20)**			0.89
				O(21)	0.30	0.30	0.30
∑s	5.57	5.7	5.74		5.71	5.63	5.66

Table S4. BVS results of V_8Mo_2

Compound	V_8Mo_2										
	V1	V2	VMo3	VMo4	VMo5		V6	V7	VMo8	VMo9	VMo10
O(1)	1.78					**O(15)**	1.76				0.49
O(2)		1.78				**O(16)**		1.74			
O(3)			1.98			**O(17)**			1.95		
O(4)				2.02		**O(18)**				2	
O(5)	0.89	0.95				**O(19)**	0.89	0.96			
O(6)	0.75		0.89		0.47	**O(20)**	0.65		0.9		
O(7)	0.78			0.92		**O(21)**	0.85			0.95	
O(8)	0.55				1.55	**O(22)**	0.54				1.53
O(9)		0.75	1.08			**O(23)**		0.69	1.07		
O(10)		0.5			1.57	**O(24)**		0.83		1.03	
O(11)		0.76		1.07		**O(25)**		0.54			1.55
O(12)			0.57	0.62	0.77	**O(26)**			0.57	0.63	0.74
O(13)	0.26	0.26	0.32	0.3	0.48	**O(27)**	0.26	0.27	0.31	0.29	0.45
O(14)			0.63	0.58	0.73	**O(28)**			0.61	0.63	0.73
∑s	5.01	5	5.47	5.51	5.57		4.95	5.03	5.41	5.53	5.49

Table S5. BVS results of **V_9Mo_1.**

Compound	V_9Mo_1									
	V1	V2	VMo3	VMo4	V5		V6	V7	VMo8	VMo9	V10
O(1)	1.8					**O(21)**	1.76				0.44
O(2)		1.81				**O(22)**		1.74			
O(3)			1.9			**O(23)**			1.82		
O(4)				1.93		**O(24)**				1.87	
O(5)	0.88	0.95				**O(25)**	0.9	0.93			
O(6)	0.74		0.84		0.44	**O(26)**	0.64		0.86		
O(7)	0.78			0.91		**O(27)**	0.88			0.9	
O(8)	0.54				1.35	**O(28)**	0.53				1.33
O(9)		0.76	1.02			**O(29)**		0.68	1.05		
O(10)		0.76		1.02		**O(30)**		0.76		1.01	
O(11)		0.5			1.36	**O(31)**		0.53			1.38
O(12)			0.55	0.61	0.7	**O(32)**			0.56	0.61	0.68
O(13)			0.64	0.56	0.67	**O(33)**			0.61	0.6	0.68
O(14)	0.27	0.26	0.32	0.3	0.45	**O(34)**	0.26	0.28	0.31	0.29	0.46

Table S6. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) of **V_1Mo_5**, **V_8Mo_2** and **V_9Mo_1**. (The atom number ratio of V and Mo in vanadomolybdic acid for ICP measurement)

Sample	Concentration/M_{Mo}(ppm)	Concentration/M_V(ppm)	Atomic number ratio V/Mo
V_1Mo_5	0.099	0.020	0.20
V_8Mo_2	0.014	0.056	4.00
V_9Mo_1	0.012	0.111	9.25

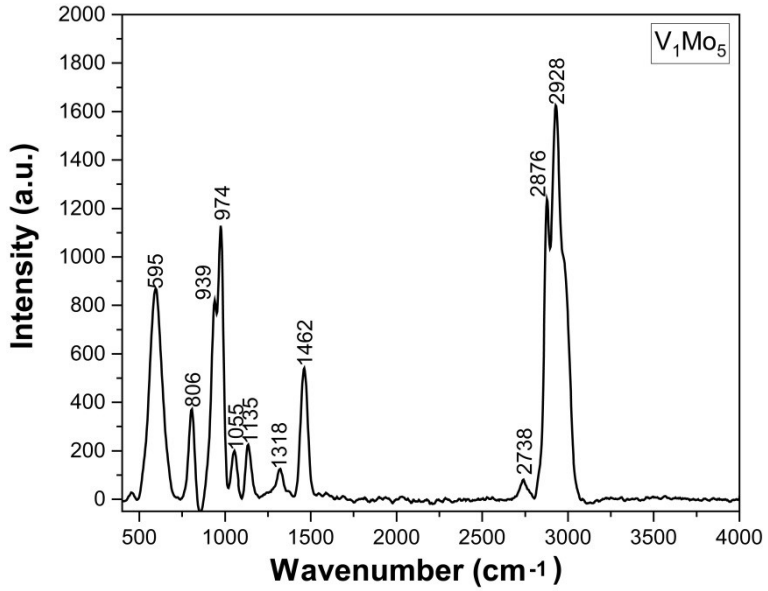

Figure S1. Raman spectrum of V_1Mo_5.

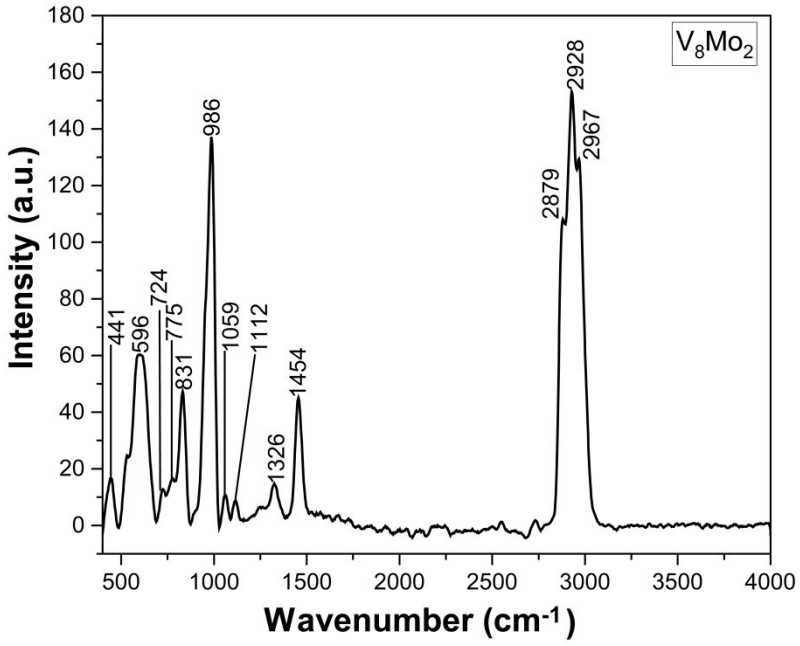

Figure S2. Raman spectrum of V_8Mo_8.

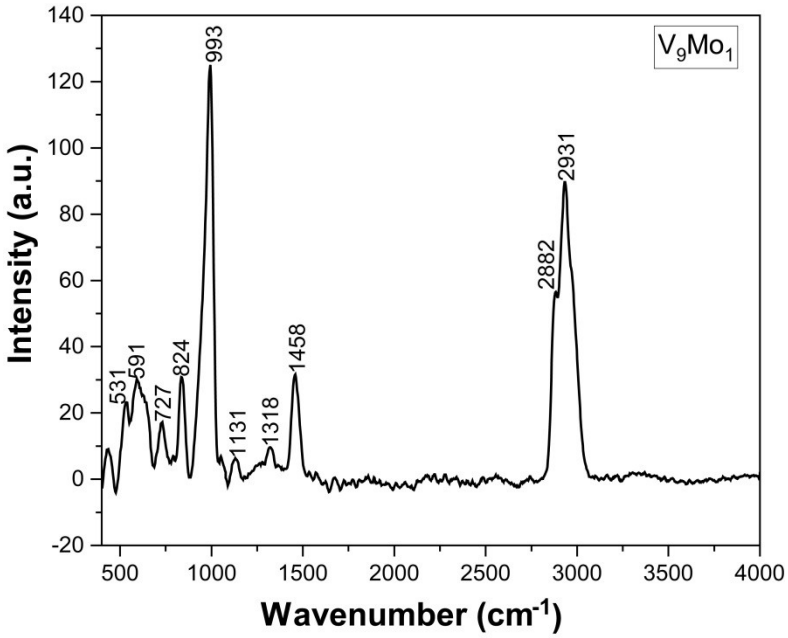

Figure S3. Raman spectrum of **V_9Mo_1.**

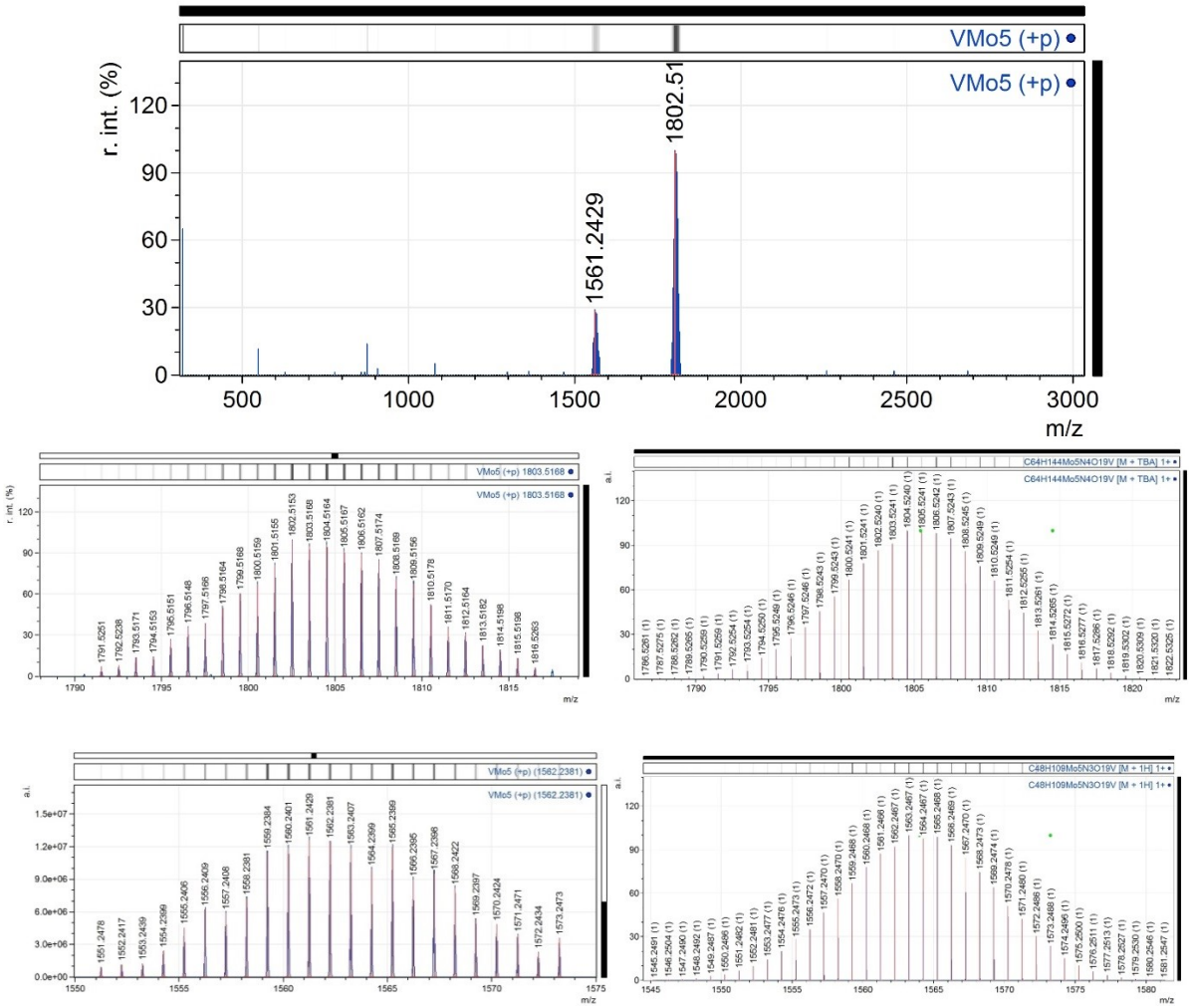

Figure S4. GC-HRMS spectrum (positive region) of $\mathbf{V_1Mo_5}$: 1561.2429 for $\{M + 1H\}^{1+}$, calcd. 1562.2467; 1803.5168 for $\{M + 1TBA\}^{1+}$, calcd. 1803.5241.

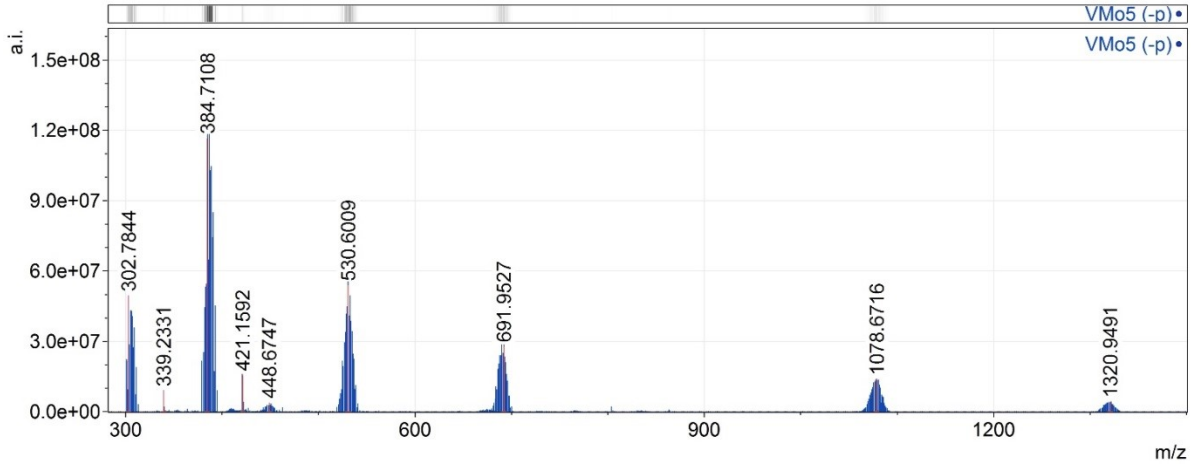

Figure S5. GC-HRMS spectrum (negative region) of $\mathbf{V_1Mo_5}$: 1320.9491 for $\{M- TBA\}^{1-}$: calcd. 1320.946; 1078.6716 for $\{M- 2TBA + H\}^{1-}$: calcd. 1078.669.

Table S7 Summary of HR MS results of $\mathbf{V_1Mo_5}$.

Negative mode of HRMS for $\mathbf{V_1Mo_5}$				
m/z	Calculated m/z	Assigned Species	Charge	Notes
302.7844	302.784	$\{HMo_2O_7\}^{1-}$	-1	fragment
384.7108	384.710	$\{VMo_2O_9\}^{1-}$	-1	fragment
421.1592	426.68	$\{Mo_3O_{11}\}^{1-}$	-1	fragment
448.6747	448.674	$\{HMo_3O_{10}\}^{1-}$	-1	fragment
530.6009	530.600	$\{VMo_3O_{12}\}^{1-}$	-1	fragment
691.9527	691.951	$\{TBA(Mo_3O_{10})\}^{1-}$	-1	fragment
1078.6716	1078.669	$\{M- 2TBA + H\}^{1-}$	-1	molecule ion
1320.9491	1320.946	$\{M- TBA\}^{1-}$	-1	molecule ion
Positive mode of HRMS for $\mathbf{V_1Mo_5}$				
1564.2419	1564.2467	$\{M + 1H\}^{1+}$	+1	molecule ion
1806.5134	1806.5242	$\{M + 1TBA\}^{1+}$	+1	molecule ion

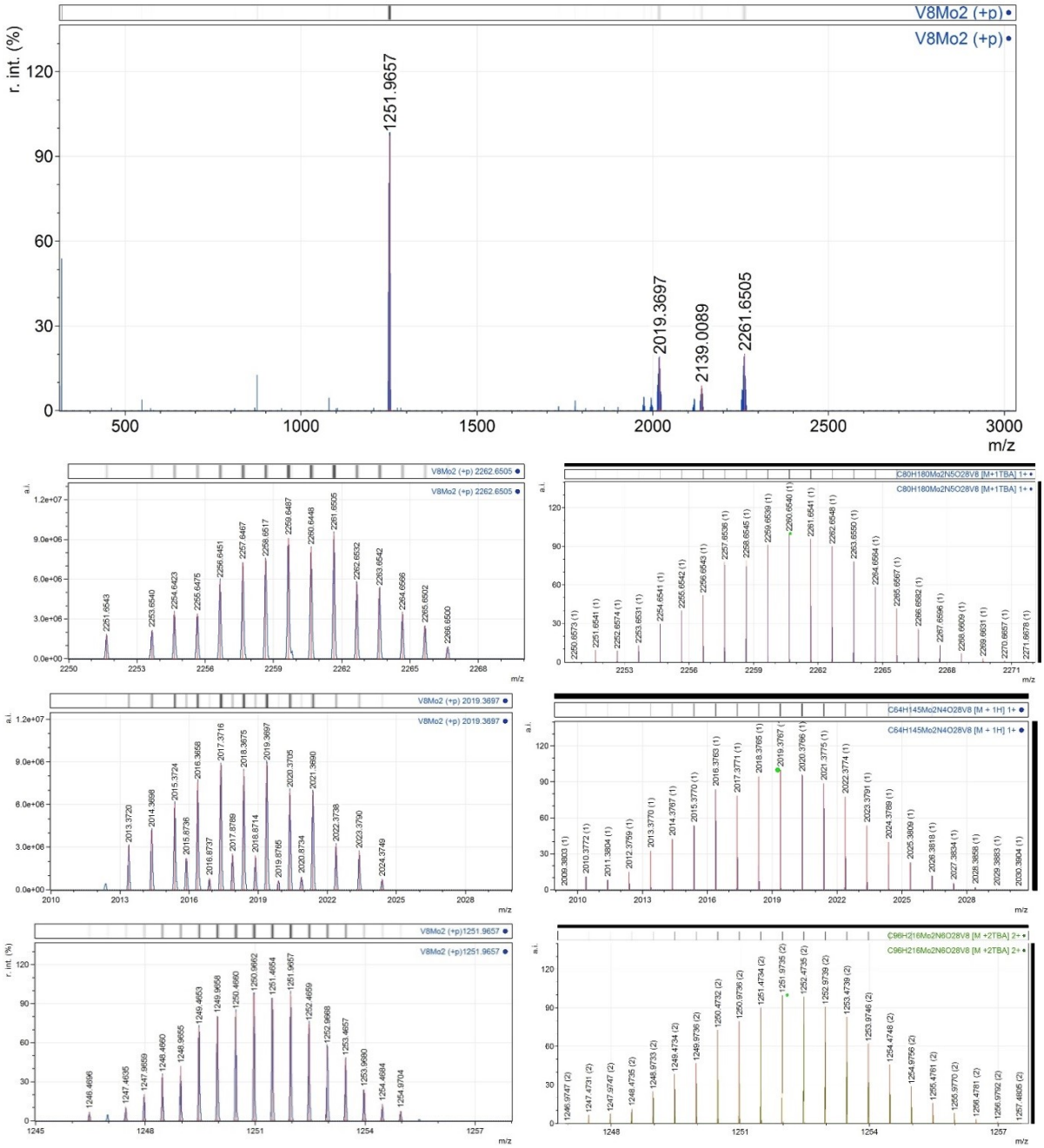

Figure S6. HRMS spectrum (positive mode) of $\mathbf{V_8Mo_2}$: 1250.9656 for $\{M + 2TBA\}^{2+}$, calcd. 1250.9736; 2018.3716 for $\{M + 1H\}^{1+}$, calcd. 2018.3765; 2261.6596 for $\{M + 1TBA\}^{1+}$: calcd. 2261.6541.

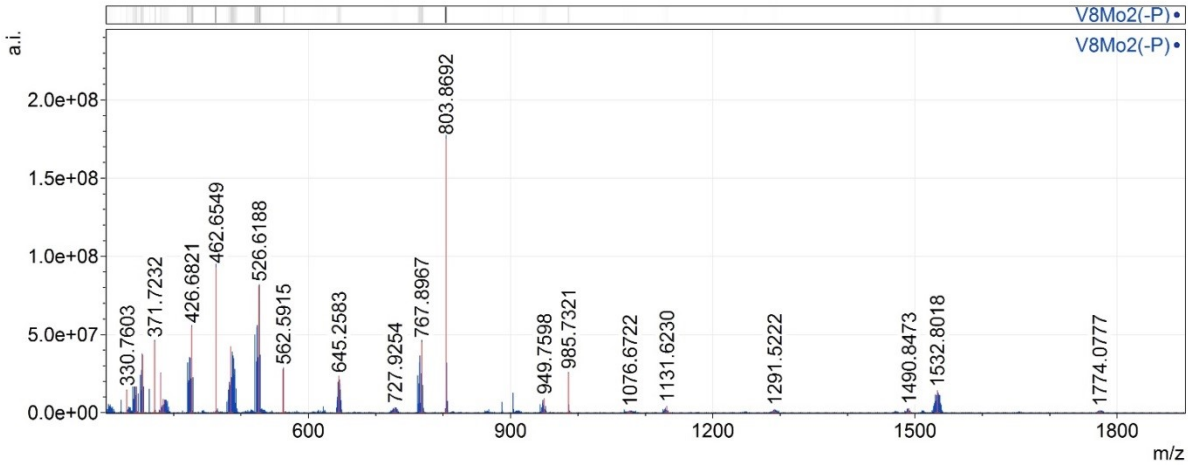

Figure S7. HRMS spectrum (negative mode) of $\mathbf{V_8Mo_2}$: 1774.0777 for $\{M - TBA\}^{1-}$, calcd. 1774.076; 1532.8018 for $\{M - 2TBA + H\}^{1-}$, calcd. 1532.799; 1291.5122 for $\{M - 3TBA + 2H\}^{1-}$, calcd. 1291.522.

Table S8 Summary of HR MS results for $\mathbf{V_8Mo_2}$.

HR MS Negative mode of $\mathbf{V_8Mo_2}$				
m/z	Calculated m/z	Assigned Species	Charge	Notes
334.7561	334.755	$\{HV_2MoO_9\}^{1-}$	-1	fragment
384.7107	384.710	$\{VMo_2O_9\}^{-1}$	-1	fragment
426.6821	426.681	$\{V_3MoO_{11}\}^{1-}$	-1	fragment
462.6549	462.654	$\{V_5O_{13}\}^{1-}$	-1	fragment
484.6474	484.646	$\{HV_2Mo_2O_{12}\}$	-1	fragment
526.6188	526.625	$\{M - 4TBA + 2H\}^{2-}$	-2	molecule ion
645.2583	646.264	$\{M - 3TBA + H\}^{2-}$	-2	molecule ion
766.3977	766.430	$\{V_5Mo_2O_{20}\}^{1-}$	-1	fragment
767.8967	767.903	$\{M - 2TBA\}^{2-}$	-1	molecule ion
867.8346	867.366	$\{HV_6Mo_2O_{23}\}^{1-}$	-1	fragment
949.7598	949.463	$\{HV_7Mo_2O_{25}\}^{1-}$	-1	fragment
1076.6722	1076.226	$\{M - 4TBA + 2H + Na\}^{1-}$	-1	molecule ion
1291.5122	1291.522	$\{M - 3TBA + 2H\}^{1-}$	-1	molecule ion
1532.8018	1532.799	$\{M - 2TBA + H\}^{1-}$	-1	molecule ion
1774.0777	1774.076	$\{M - TBA\}^{1-}$	-1	molecule ion
HR MS positive mode of $\mathbf{V_8Mo_2}$				
m/z	Calculated m/z	Assigned Species	Charge	Notes
1250.9656	1250.9736	$\{M + 2TBA\}^{2+}$	+2	molecule ion
2018.3716	2018.3765	$\{M + 1H\}^{1+}$	+1	molecule ion
2261.6596	2261.6541	$\{M + 1TBA\}^{1+}$	+1	molecule ion

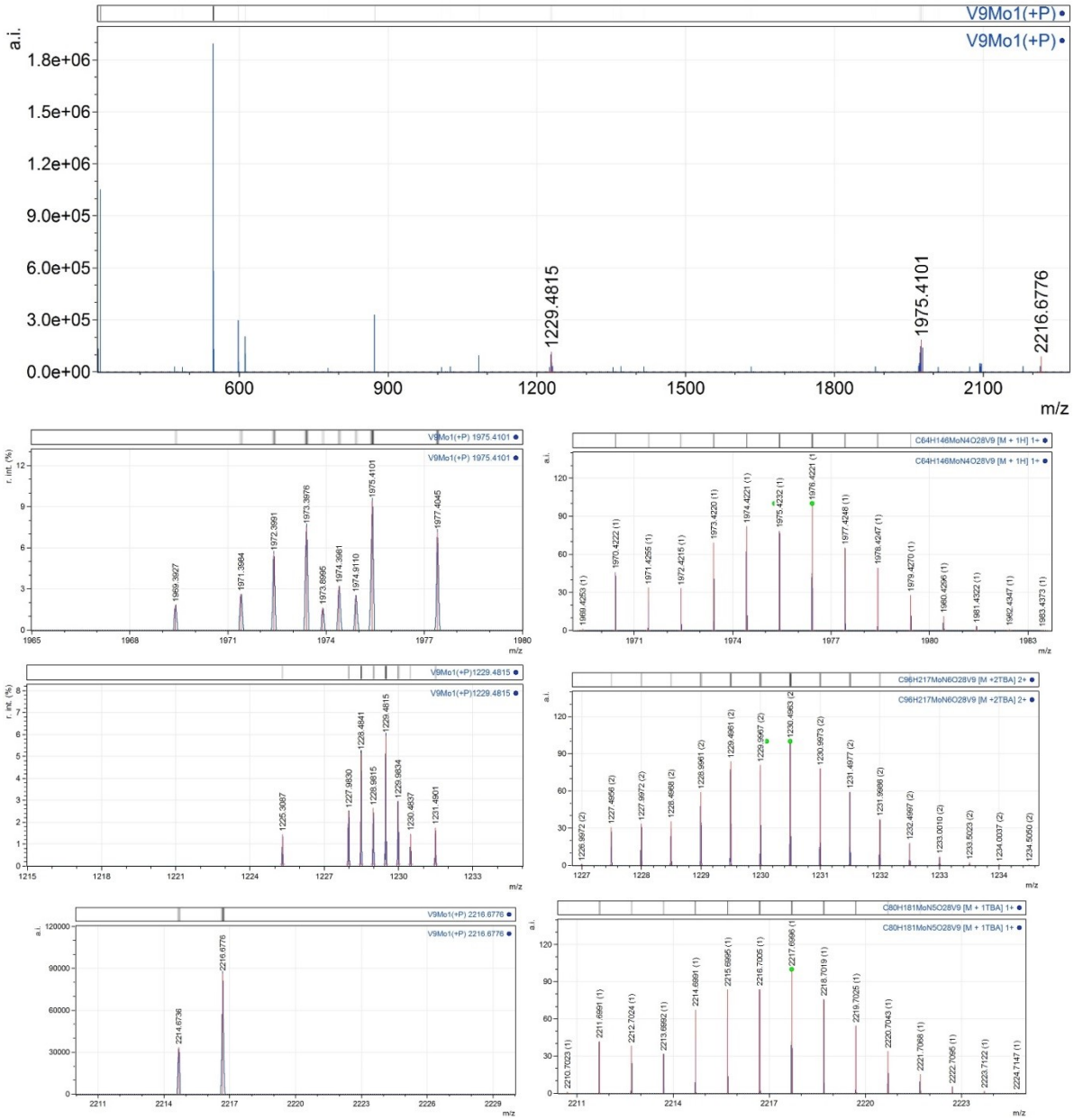

Figure S8. HR MS spectrum (positive mode) of $\mathbf{V_9Mo_1}$: 1229.4815 for $\{M + 2TBA\}^{2+}$, calcd. 1229.1961; 1975.4501 for $\{M + H\}^{1+}$, calcd. 1975.4231; 2216.6776 for $\{M + TBA\}^{1+}$, calcd. 2216.7005.

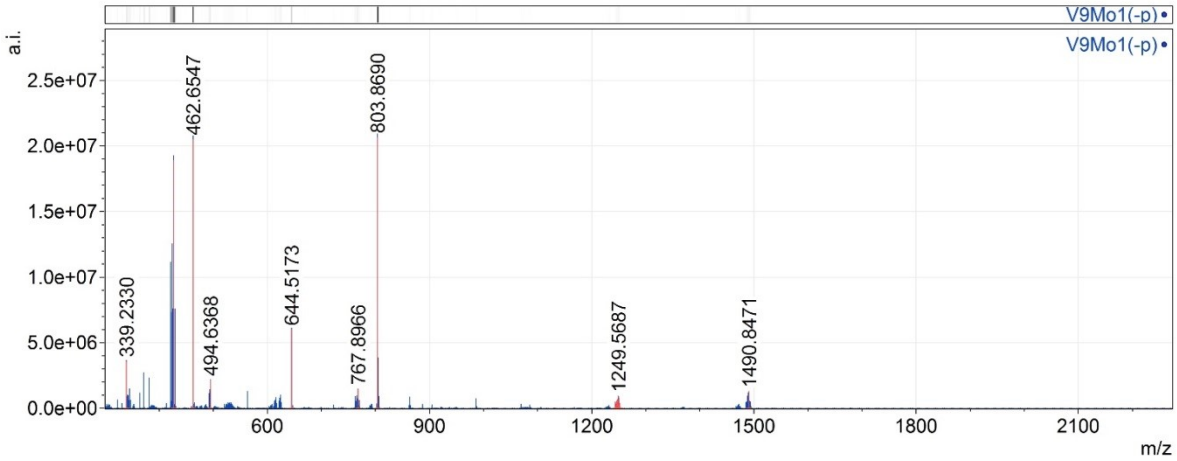

Figure S9. HR MS spectrum (negative mode) of **V_9Mo_1**: 1490.8471 for $\{M- 2TBA + H\}^{1-}$, calcd. 1490.8485; 1249.5687 for $\{M- 3TBA + 2H\}^{1-}$, calcd. 1249.5673.

Table S9 Summary of HR MS results for **V_9Mo_1.**

HR MS Negative mode of **V_9Mo_1**				
m/z	Calculated m/z	Assigned Species	Charge	Notes
339.2330	339.760	$\{HV_2MoO_9\}^{1-}$	-1	ragment
426.6818	426.68	$\{V_3MoO_{11}\}^{1-}$	-1	fragment
462.6547	462.65	$\{V_5O_{13}\}^{1-}$	-1	fragment
494.6368	494.628	$\{HV_4MoO_{12}\}$	-1	fragment
644.5173	644.516	$\{V_7O_{18}\}^{1-}$	-1	fragment
1249.5687	1249.5673	$\{M- 3TBA + 2H\}^{1-}$	-1	molecule ion
1490.8471	1490.8485	$\{M- 2TBA + H\}^{1-}$	-1	molecule ion
HR MS Negative mode of **V_9Mo_1**				
m/z	Calculated m/z	Assigned Species	Charge	Notes
1229.4815	1229.1961	$\{M + 2TBA\}^{2+}$	+2	molecule ion
1975.4501	1975.4231	$\{M + H\}^{1+}$	+1	molecule ion
2216.6776	2216.7005	$\{M + TBA\}^{1+}$	+1	molecule ion

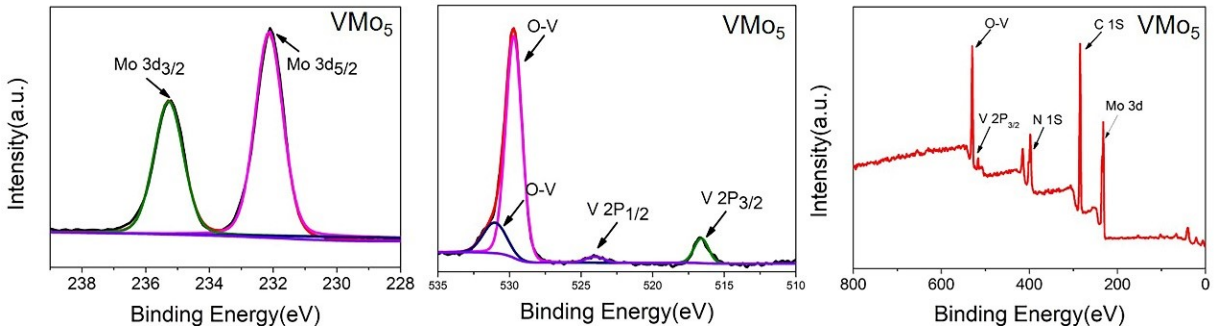

Figure S10. XPS spectrum of V_1Mo_5.

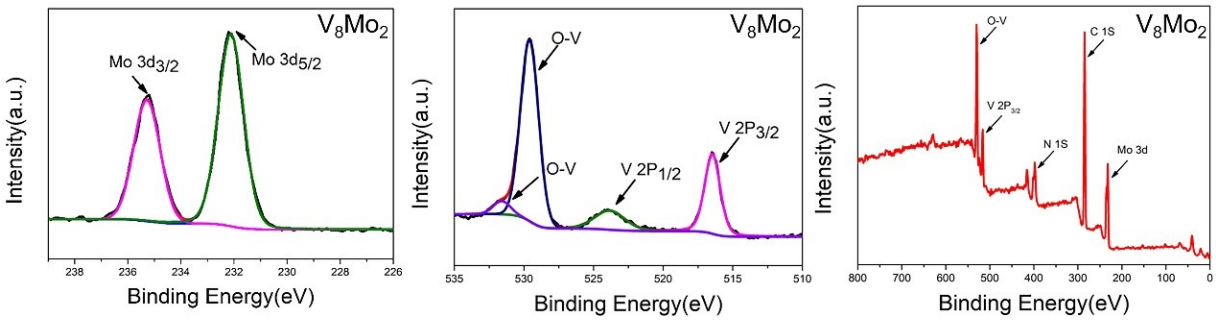

Figure S11. XPS spectrum of V_8Mo_2.

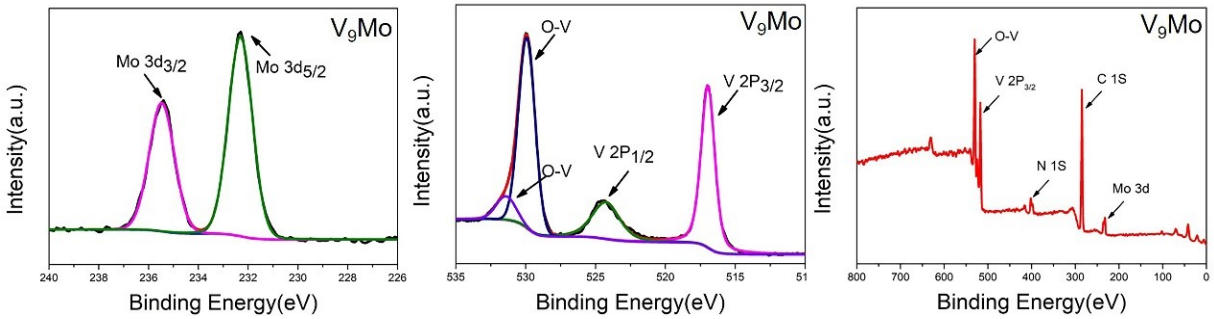

Figure S12. XPS spectrum of V_9Mo_1.

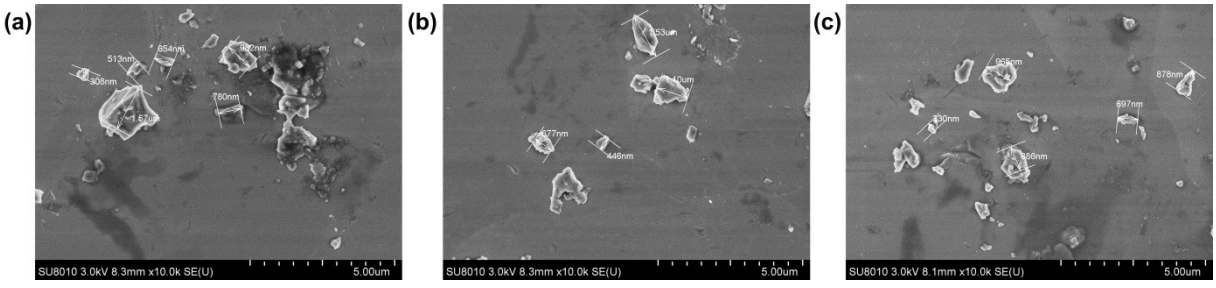

Figure S13.SEM images of V_1Mo_5, V_8Mo_2 and V_9Mo_1.

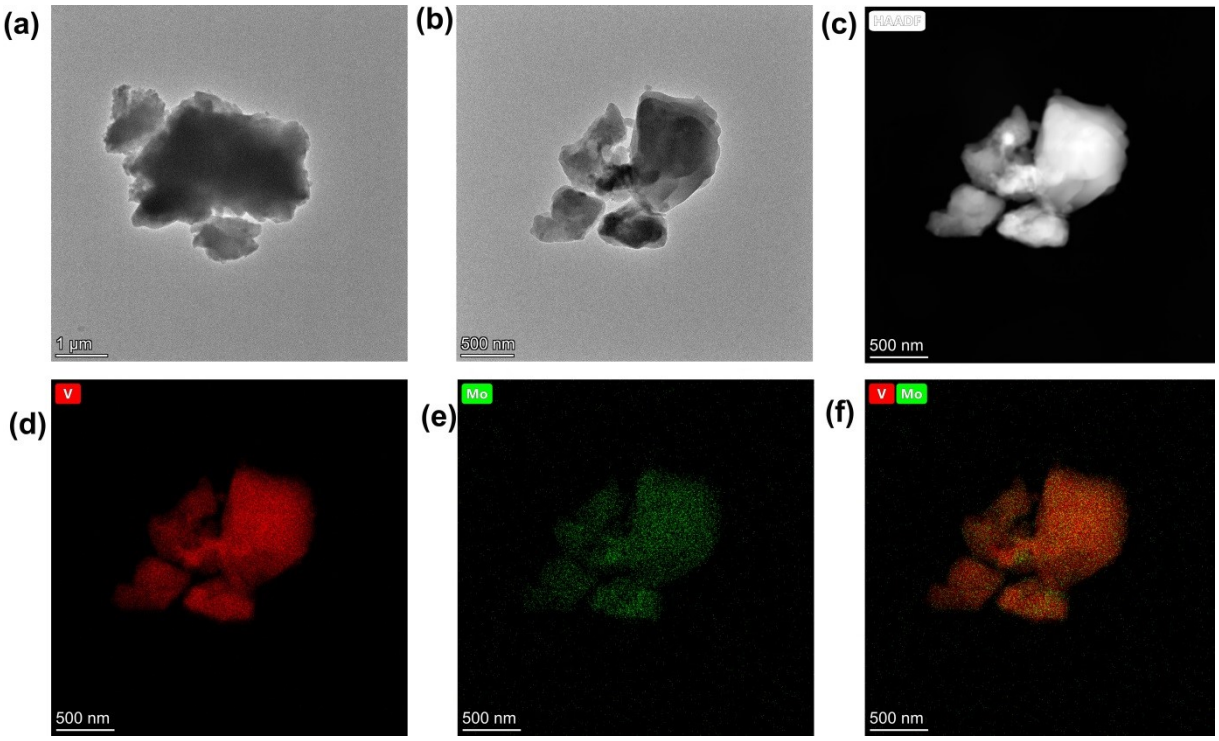

Figure S14. TEM images of $\mathbf{V_8Mo_2}$: (a), (b) TEM images, (c) HAADF-STEM image; (d) Corresponding EDX mapping of V and Mo distribution; (f) composite of V/ Mo.

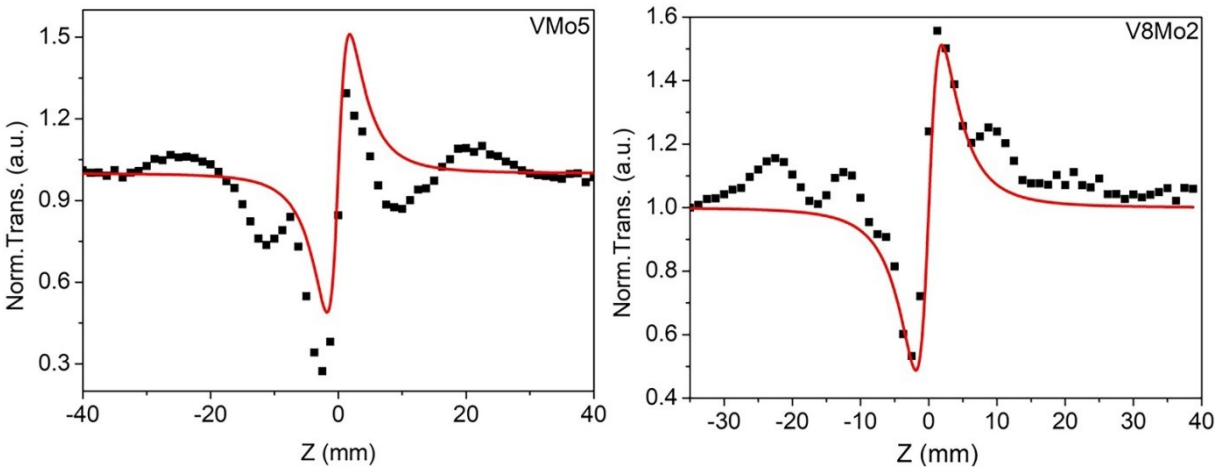

Figure S15. The closed-aperture Z-scan result of $\mathbf{V_1Mo_5}$ and $\mathbf{V_8Mo_2}$.

Table S10. NLO coefficients of $\mathbf{V_{10}}$, $\mathbf{V_1Mo_5}$, $\mathbf{V_8Mo_2}$ and $\mathbf{V_9Mo_1}$ in propanetriol at the laser of 532 and 1064 nm.

Compounds	λ[nm]	T_{min}	β_{eff} [cm GW^{-1}]	Im χ(3) [esu]	n_2
$\mathbf{V_1Mo_5}$	532	0.75	60.16	2.9×10^{-8}	1.08×10^{-5}
$\mathbf{V_8Mo_2}$		0.50	123.79	6.0×10^{-8}	8.9×10^{-6}
$\mathbf{V_9Mo_1}$		0.06	691.79	3.3×10^{-7}	9.95×10^{-6}
$\mathbf{V_{10}}$		0.26	202.63	9.8×10^{-8}	
$\mathbf{V_1Mo_5}$	1064	0.85	80.19	7.8×10^{-8}	
$\mathbf{V_8Mo_2}$		0.53	127.98	1.24×10^{-7}	
$\mathbf{V_9Mo_1}$		0.22	292.52	2.8×10^{-7}	
$\mathbf{V_{10}}$		0.80	69.59	6.8×10^{-8}	

Calculation Details of NLO Coefficients

The measured Z-scan curves were fitted using the following expressions: [3]

$$T(z) = 1 - \beta I_0 L_{eff}/[2\sqrt{2}\left(1+\frac{z^2}{z_0^2}\right)] = 1 - [1 - T(z=0)]/(1+\frac{z^2}{z_0^2})$$

$$L_{eff} = [1 - \exp(-\alpha L)]/\alpha$$

Where β is nonlinear absorption coefficient, I_0 is the energy density at the focus (z=0), L_{eff} is the effective thickness of the sample; α is the linear absorption coefficient and L is the thickness of sample. The equation of T can be fitted and calculated to get the β values.

The imaginary parts of the third order nonlinear optical susceptibility $\chi^{(3)}$ are determined from the following equation: [4]

$$Im\ \chi^{(3)} = \frac{n_0^2 \varepsilon_0 c \lambda \beta}{2\pi}$$

where n_0 is the linear refractive index, ε_0 is the permittivity of free space, c is the speed of light, λ is the laser wavelength and β is nonlinear absorption coefficient.

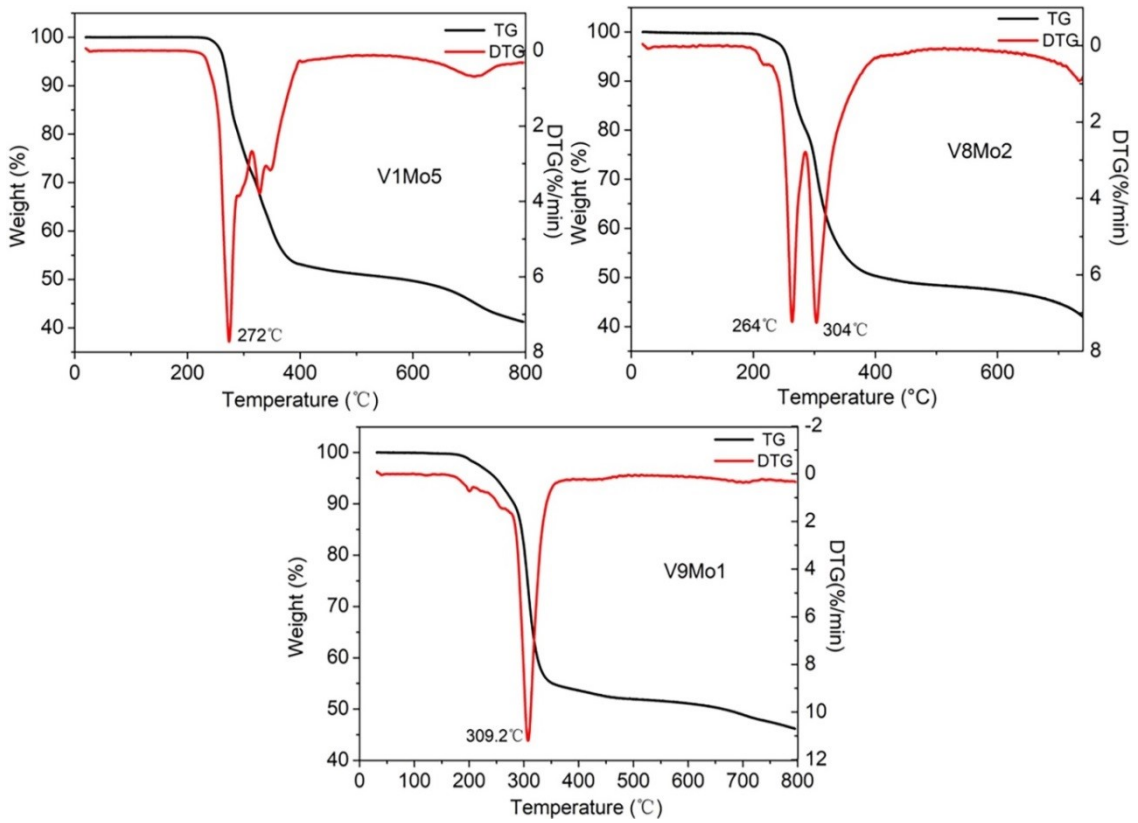

Figure S17. TG and DTG curves of $\mathbf{V_1Mo_5}$, $\mathbf{V_8Mo_2}$ and $\mathbf{V_9Mo_1}$.

Thermo gravimetric analyzer (TGA) was applied to explore the thermal stability of $\mathbf{V_1Mo_5}$, $\mathbf{V_8Mo_2}$ and $\mathbf{V_9Mo_1}$ using the temperature rate of 10 °C/min at the N_2 atmosphere. As shown in Fig S11, $\mathbf{V_1Mo_5}$ has a negligible weight loss of about 0.3% before 220°C. A rapid weight loss (46.6%) occurs between 220~390°C, which is corresponding to the loss of three TBA cations (46.2%). $\mathbf{V_8Mo_2}$ displays a very small weight loss ca. 0.9% before 217°C, which is less than the theoretical loss of two acetonitrile solvent molecules (3.8%) because $\mathbf{V_8Mo_2}$ is easy to loss its crystallized solvent molecules. A rapid weight loss (48.3%) is followed between 217~390°C, which is well matched with the loss of four TBA cations (48.1%). Compound **3** has a slow weight loss before 195 °C (ca. 0.09%), which is also less than the theoretical weight loss of two acetonitrile solvent molecules (3.99%), indicating that $\mathbf{V_9Mo_1}$ had lost two crystallized acetonitrile molecules before the TG test. A rapid weight loss (ca. 45.3%) associated with the loss of four TBA cation (47.2%) is found between 195 ~ 395 °C.

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