Supporting Information

Optical properties regularities in the family of {Mo$_6$I$_8$} aquahydroxo complexes

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Content

FTIR spectra, XRPD patterns, and TGA curves
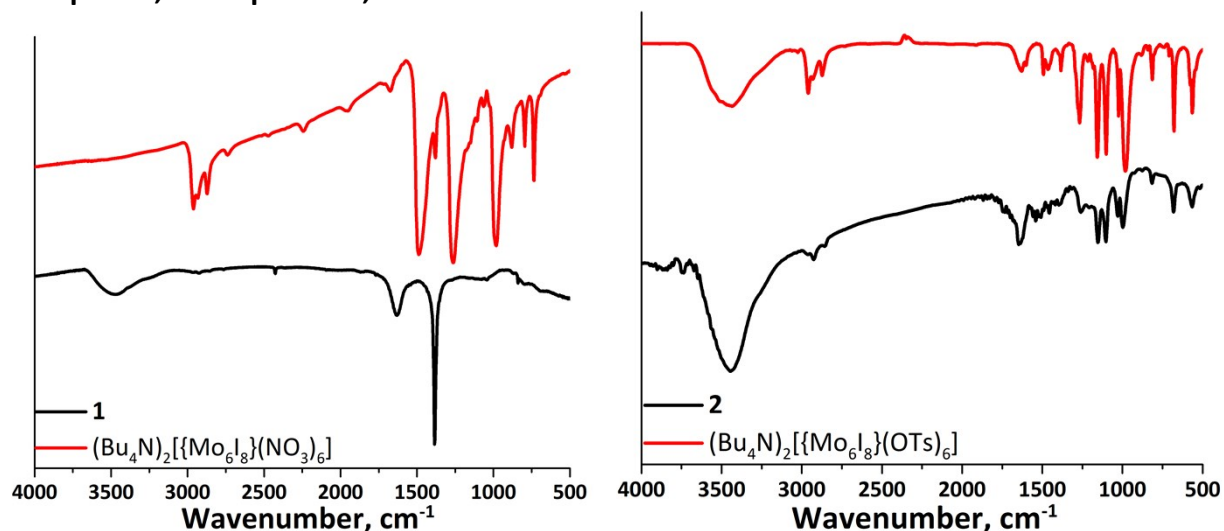

Figure 1S. FTIR spectra of **1-NO₃** (*left*) and **1-OTs** (*right*) in comparison with initial clusters.
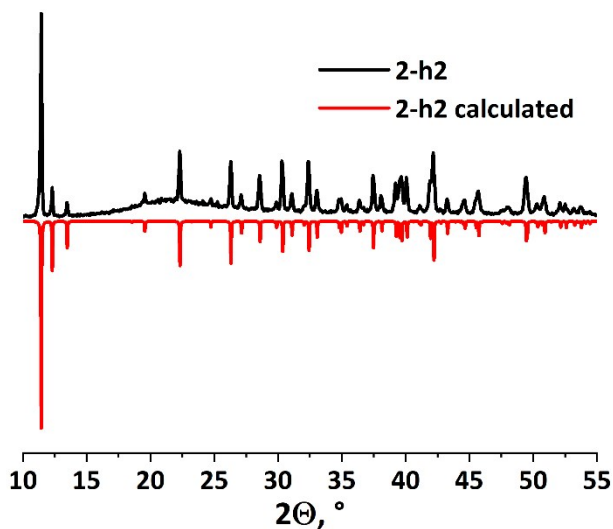
Figure 2S. XRPD pattern of **2-h2** in comparison with calculated from the crystal structures of [{Mo$_6$I$_8$}(H$_2$O)$_2$(OH)$_4$]·2H$_2$O.
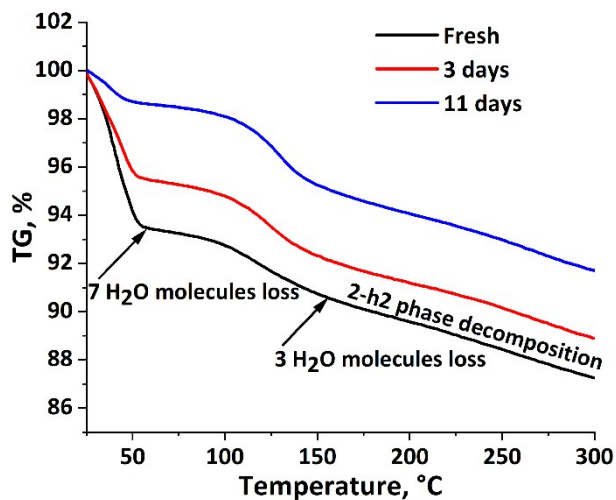

Figure 3S. TGA curves of **2-h2** and **2-h12^{new}** (fresh and 3 and 11 days old). Heating rates of 10 °C min^{-1}.

Table 1S. Crystallographic data, data collection and refinement parameters.

	1-NO$_3$	1-OTs	2-h12^{new}
Empirical formula	H$_{16}$I$_8$Mo$_6$N$_2$O$_{15}$	C$_{14}$H$_{28}$I$_8$Mo$_6$O$_{14}$S$_2$	H$_{32}$I$_8$Mo$_6$O$_{18}$
Formula weight	1874.99	2075.32	1911.09
Temperature (K)	150(2)	150(2)	150(2)
Crystal size (mm^3)	0.120 × 0.100 × 0.030	0.160 × 0.130 × 0.040	0.085 × 0.085 × 0.035
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
Z	2	1	1
Unit cell dimensions			
a (Å)	10.5553(3)	9.447(1)	9.4284(9)
b (Å)	11.5145(3)	9.459(1)	9.799(1)
c (Å)	12.9195(3)	11.504(1)	10.008(1)
α (°)	78.837(1)	77.300(3)	73.929(4)
β (°)	78.265(1)	79.348(3)	67.566(4)
γ (°)	67.511(1)	73.852(3)	88.598(4)
Volume (Å^3)	1408.80(6)	954.8(2)	817.8(1)
D$_{calcd.}$ (g·cm^{-3})	4.420	3.609	3.815
μ (mm^{-1})	11.411	8.539	9.837
θ range (°)	1.623 – 27.619	1.831 – 27.157	2.300 – 36.312
Index ranges	−12 ≤ h ≤ 13 −11 ≤ k ≤ 14 −13 ≤ l ≤ 16	−12 ≤ h ≤ 12 −12 ≤ k ≤ 12 −14 ≤ l ≤ 14	−15 ≤ h ≤ 12 −16 ≤ k ≤ 14 −16 ≤ l ≤ 13
Reflections collected	12016	7699	22858
Independent reflections	6450 (R$_{int}$ = 0.0293)	4143 (R$_{int}$ = 0.0337)	7293 (R$_{int}$ = 0.0411)
Data / restraints / parameters	6450 / 19 / 342	4143 / 6 / 210	7293 / 0 / 159
R[$F^2 > 2\sigma(F^2)$]	R$_1$ = 0.0185 wR$_2$ = 0.0466	R$_1$ = 0.0634 wR$_2$ = 0.1967	R$_1$ = 0.0357 wR$_2$ = 0.0645
R(F^2) (all data)	R$_1$ = 0.0342 wR$_2$ = 0.0492	R$_1$ = 0.0680 wR$_2$ = 0.2010	R$_1$ = 0.0504 wR$_2$ = 0.0692
Goodness-of-fit on F^2	1.037	1.063	1.018
Δρ$_{max}$, Δρ$_{min}$ (e·Å^{-3})	1.135, −0.866	2.813, −7.017	1.462, −2.278

Table 2S. Selected interatomic distances (Å).

	1-NO$_3$	1-OTs	2-h12^{new}
Mo-Mo	2.6509(4)–2.6751(4)	2.647(1)–2.662(1)	2.6566(5)–2.6670(5)
Mo-I	2.7599(4)–2.8049(4)	2.781(1)–2.801(1)	2.787(5)–2.8057(5)
Mo-O	2.113(2)–2.189(3)	2.053(7)–2.175(8)	2.089(3)–2.192(3)

Representation of the layered structure in 1-NO₃ and 1-OTs and absorption spectra of aqueous solutions of 1-NO₃ at different pH
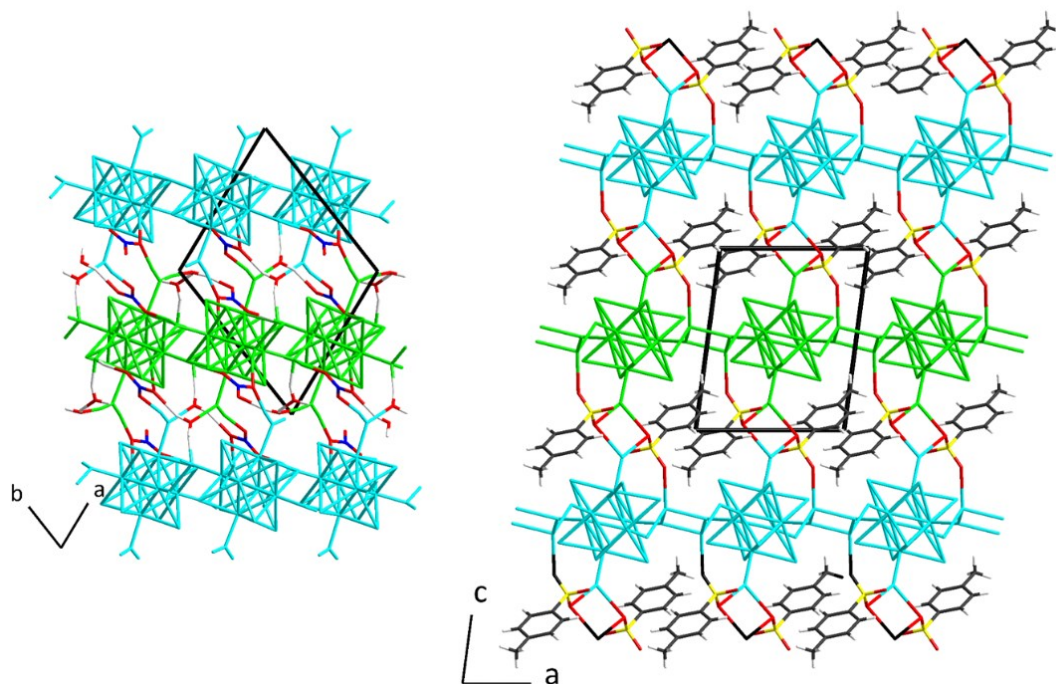

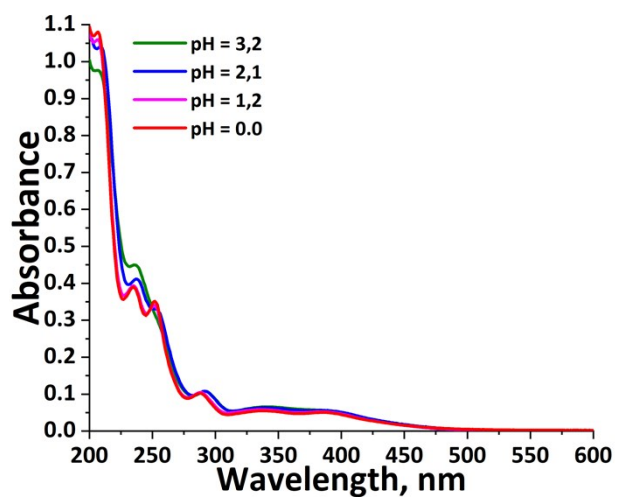**Figure 4S.** The side view on the layers in **1-NO₃** (*left*) and **1-OTs** (*right*).

Figure 5S. Absorption spectra of aqueous solutions of **1-NO₃** at different pH (3.1, 2.1, 1.2 and 0).

Selected parameters of crystal structure and emission of the clusters and deconvolution of the emission spectra of 1-NO$_3$ and 1-OTs in solid state

Table 3S. Selected parameters of crystal structure and emission of the clusters.

Cluster	Number of direct hydrogen contacts	d_{calc}, g cm^{-3}	Cluster-cluster contacts, Å	λ_{em}, nm	Relative intensity, a.u.	S_{int}, a.u.[#]
1-OTs	0	3.609	9.447; 9.459; 11.504	661	395	50239
2-h12^{new}	0	3.815	9.428; 9.799; 10.008	693	274	7887
1-NO$_3$	4	4.420	8.885; 8.945; 10.555	705	66	29261
2-h2	6	4.932	9.138; 9.634	706	18	1889

[#]S_{int} is integrated emission intensity (area under the curve)
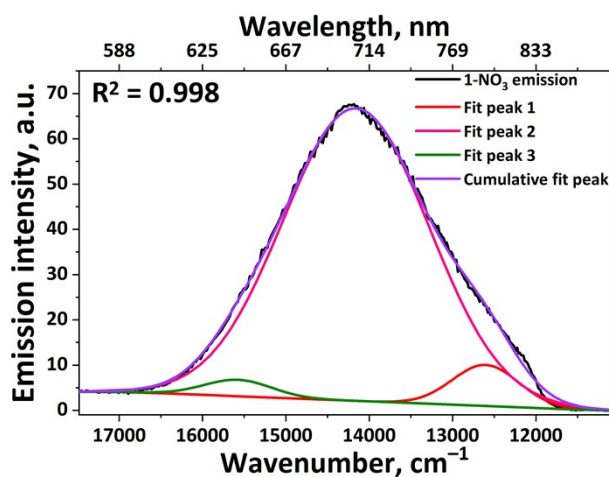
Figure 6S. Deconvolution of the emission spectra of **1-NO$_3$** in solid state.
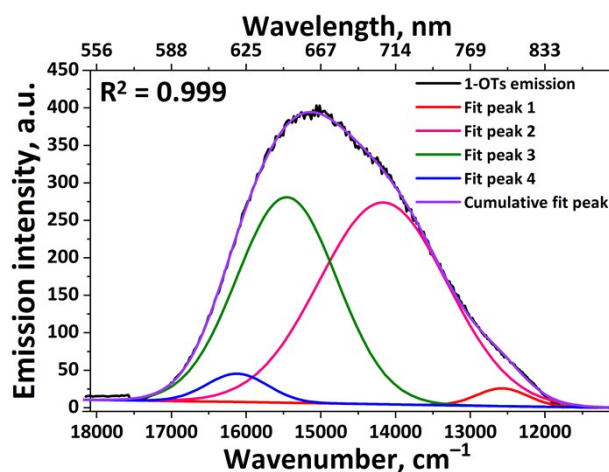
Figure 7S. Deconvolution of the emission spectra of **1-OTs** in solid state.

Deconvolution of the emission spectra of 2-h2 and 2-h12^{new} in solid state
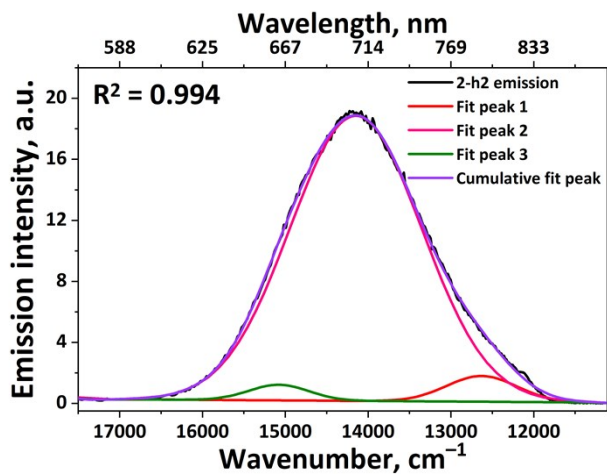

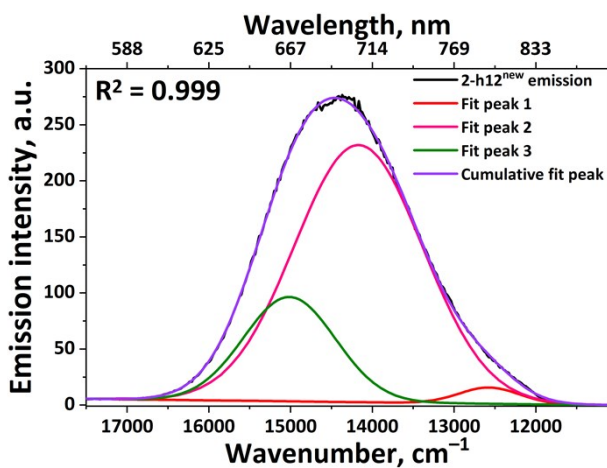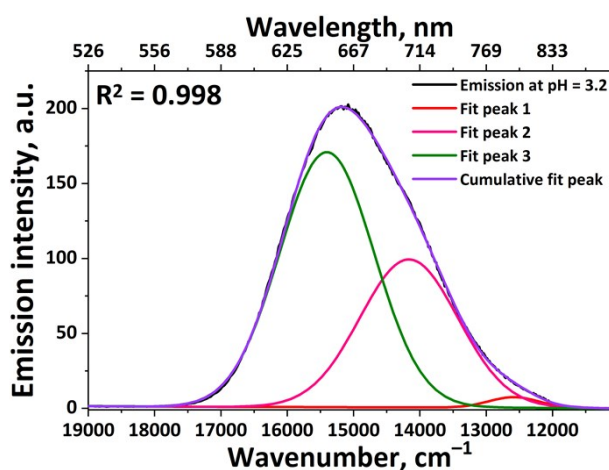**Figure 8S.** Deconvolution of the emission spectra of **2-h2** in solid state.

Figure 9S. Deconvolution of the emission spectra of **2-h12^{new}** in solid state.
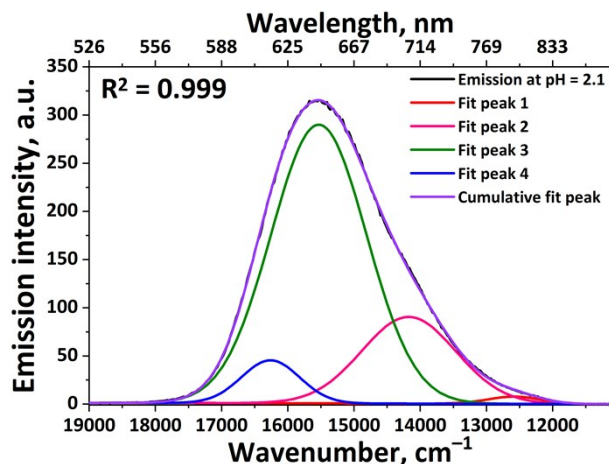
Parameters of deconvolution of emission spectra in solid state and deconvolution of the emission spectra of 1-NO$_3$ in aqueous solution at pH = 3.2 and 2.1

Table 4S. Overall emission maximum (λ_{em}), integrated emission intensity (S_{int}), peak positions, FWHM, relative contributions of the peaks integrated area to the area of cumulative peak in %, and coefficient of determination of cumulative peak (R^2) for clusters in solid state.

Parameter	1-OTs	1-NO$_3$	2-h12^{new}	2-h2
λ_{em}, nm; (cm^{-1})	661; (15135)	705; (14180)	693; (14416)	706, (14164)
λ_{max1}, nm; (cm^{-1})	620; (16118)	–	–	–
λ_{max2}, nm; (cm^{-1})	647; (15455)	642 (15578)	666; (15013)	663; (15077)
λ_{max3}, nm; (cm^{-1})	706; (14165)	706; (14159)	706; (14168)	707; (14147)
λ_{max4}, nm; (cm^{-1})	795; (12571)	793; (12605)	796; (12571)	792 (12629)
FWHM 1	958	–	–	–
FWHM 2	1575	948	1321	851
FWHM 3	2016	2062	1848	1868
FWHM 4	795	936	865	998
Cont. 1, %	3.51	–	–	–
Cont. 2, %	41.96	2.37	21.98	2.32
Cont. 3, %	52.70	91.79	75.78	93.19
Cont. 4, %	1.83	5.84	2.24	4.49
R^2	0.999	0.998	0.999	0.994

Figure 10S. Deconvolution of the emission spectra of **1-NO$_3$** in aqueous solution at pH = 3.2.

Figure 11S. Deconvolution of the emission spectra of **1-NO$_3$** in aqueous solution at pH = 2.1.

Deconvolution of the emission spectra of 1-NO$_3$ in aqueous solution at pH = 1.2 and 0.0
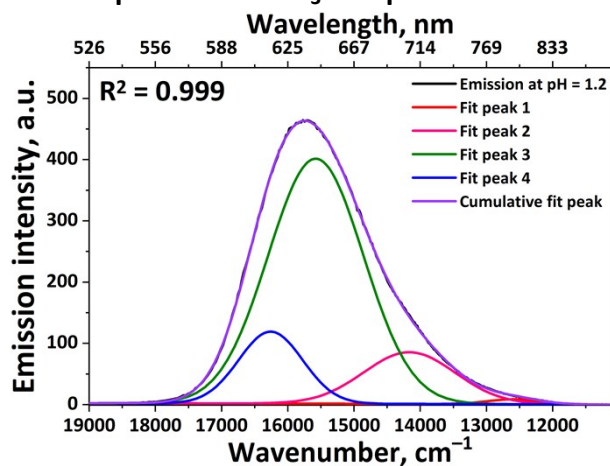

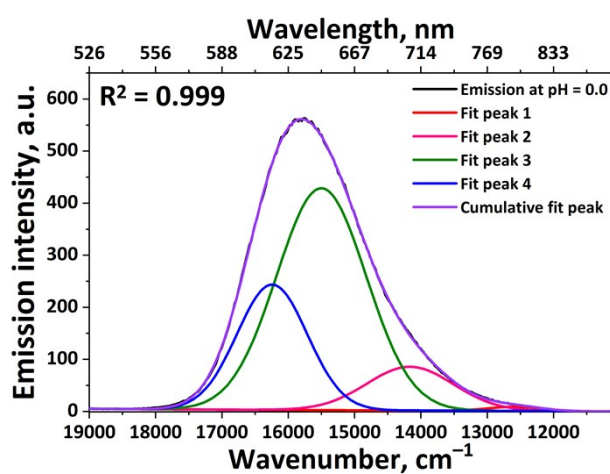**Figure 12S.** Deconvolution of the emission spectra of **1-NO$_3$** in aqueous solution at pH = 1.2.

Figure 13S. Deconvolution of the emission spectra of **1-NO$_3$** in aqueous solution at pH = 0.0.

Parameters of deconvolution of emission spectra of 1-NO$_3$ in in aqueous solution at different pH

Table 5S. Overall emission maximum (λ_{em}), integrated emission intensity (S_{int}), peak positions, FWHM, relative contributions of the peaks integrated area to the area of cumulative peak in %, and coefficient of determination of cumulative peak (R^2) for **1-NO$_3$** in aqueous solution at different pH.

Parameter	pH = 3.2	pH = 2.1	pH = 1.2	pH = 0.0
λ_{em}, nm;	658;	643;	636;	633,
(cm^{-1})	(15198)	(15552)	(15723)	(15798)
S_{int}, a.u.$^{\#}$	22324	31797	42967	49345
λ_{max1}, nm;		615;	615;	616;
(cm^{-1})	-	(16261)	(16258)	(16242)
λ_{max2}, nm;	649;	644;	642;	645;
(cm^{-1})	(15402)	(15532)	(15577)	(15500)
λ_{max3}, nm;	706;	706;	706;	706;
(cm^{-1})	(14166)	(14173)	(14167)	(14164)
λ_{max4}, nm;	795;	795;	795;	795;
(cm^{-1})	(12583)	(12577)	(12579)	(12575)
FWHM 1	-	1031	1137	1245
FWHM 2	1676	1696	1690	1588
FWHM 3	1738	1673	1628	1541
FWHM 4	884	935	934	947
Cont. 1, %	-	6.61	13.99	26.91
Cont. 2, %	61.60	70.70	70.83	60.80
Cont. 3, %	37.06	21.67	14.40	11.61
Cont. 4, %	1.34	1.01	0.78	0.68
R^2	0.998	0.999	0.999	0.999

$^{\#}S_{int}$ is integrated emission intensity (area under the curve)