Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

"On the influence of the titanium source on the composition and structure of novel titanoniobates "

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Content

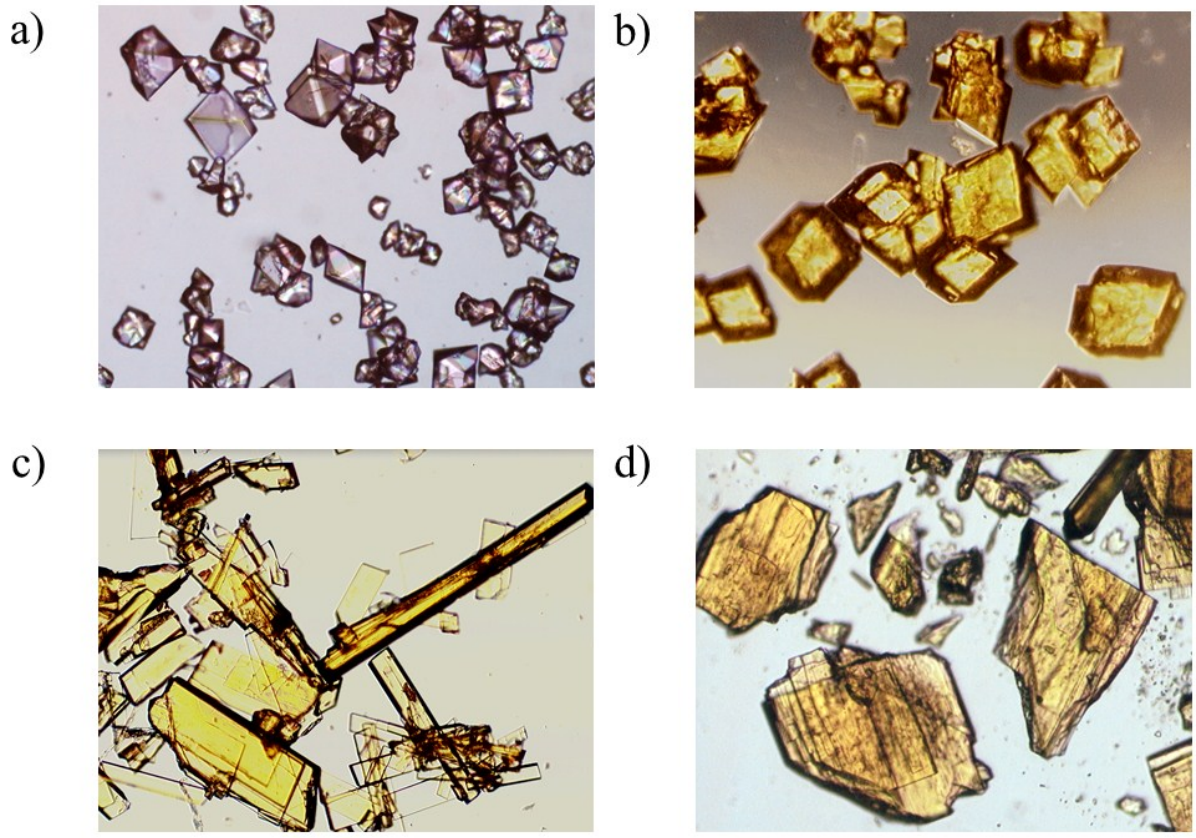
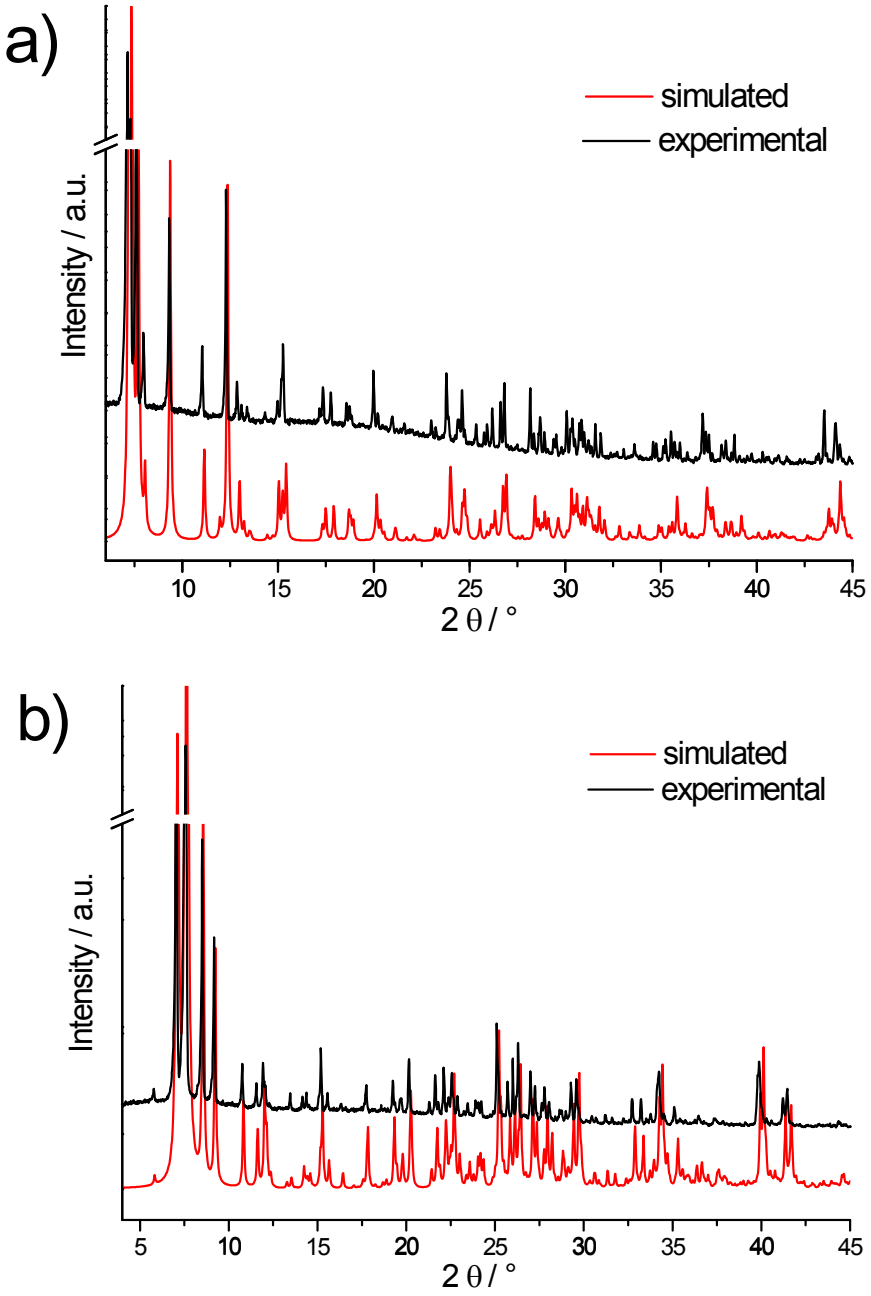
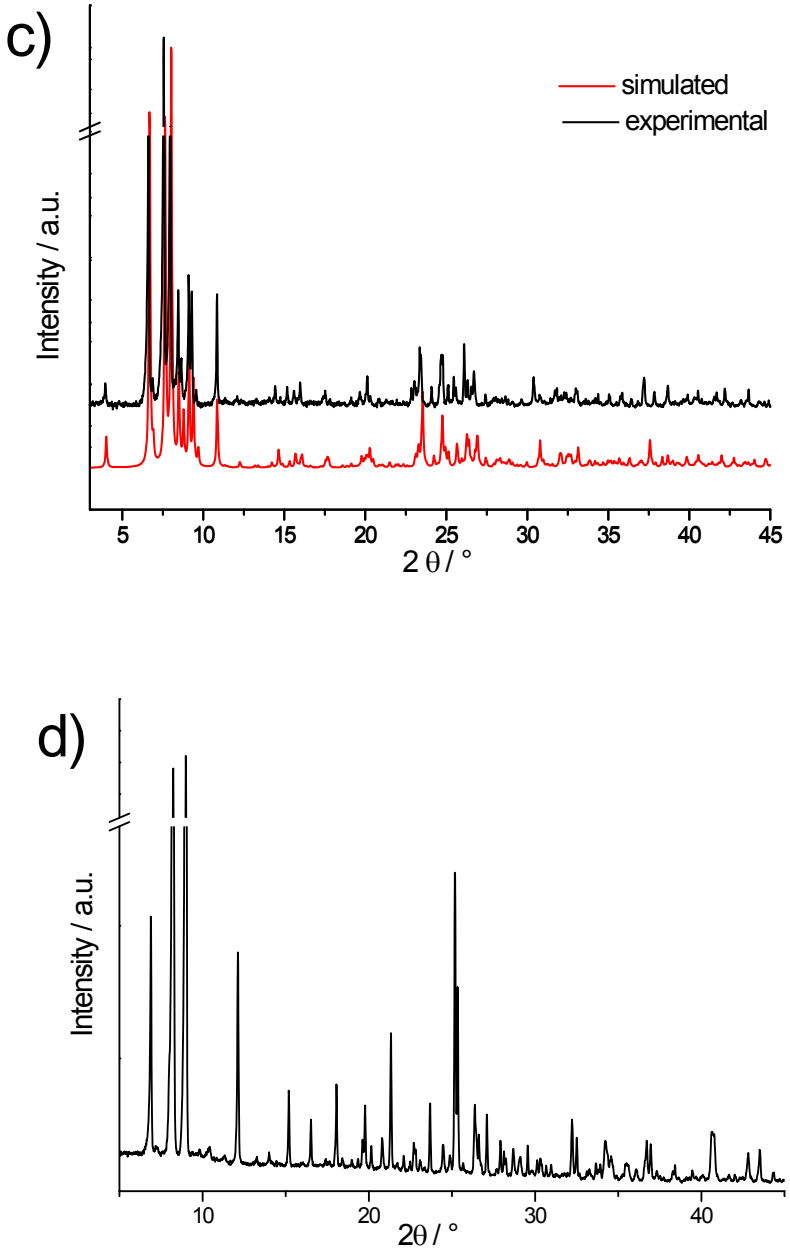


Figure S1a-d: Optical micrographs of the crystals of $\{[Ni(cyclam)]_4[Ti_2Nb_8O_{28}]\}_n \cdot 22nH_2O$ (a), $K[Ni(cyclam)]_3[TiNb_9O_{28}] \cdot 18H_2O$ (b), $K[Ni(cyclam)]_3[TiNb_9O_{28}] \cdot 14H_2O$ (c) and $K[Ni(cyclam)]_3[TiNb_9O_{28}] \cdot \sim 10H_2O$ (d)

Table S1: Selected crystal data for all compounds and details of the structure refinement.

	Compound **I**	Compound **II**	Compound **III**
Sum formula	$C_{40}H_{140}N_{16}Ni_4Nb_8Ti_2O_{50}$	$C_{30}H_{108}KN_{12}Nb_9Ni_3O_{46}Ti$	$C_{30}H_{100}KN_{12}Nb_9Ni_3O_{42}Ti$
Crystal system	monoclinic	monoclinic	triclinic
Space group	*C*2/m	*C*2/c	*P*-1
a / Å	18.8775(6)	25.3130(6)	11.6781(5)
b / Å	21.9384(5)	19.1246(5)	13.7488(8)
c / Å	14.6624(4)	15.9741(4)	22.6762(13)
α / °	90	90	103.762(4)
β / °	128.456(2)	100.847(2)	90.404(4)
γ / °	90	90	98.135(4)
V / Å^3	4755.1(2)	7594.9(3)	3497.6(3)
Z	2	4	2
Formula weight / g · mol^{-1}	2719.59	2472.44	2400.53
$\rho_{calc.}$ / g · cm^{-3}	1.899	2.197	2.279
λ / Å	0.71073	0.71073	0.71073
Scan mode	Omega scan	Omega scan	Omega scan
2θ range / °	1.661 ≤ θ ≤ 27.005	1.343 ≤ θ ≤ 27.005	1.542 ≤ θ ≤ 27.005
Crystal dimensions / mm	0.06 x 0.11 x 0.16	0.07 x 0.09 x 0.12	0.06 x 0.09 x 0.12
Crystal colour	pale purple	yellow	yellow
Temperature / K	170(2)	170(2)	170(2)
Index range	-24 ≤ h ≤ 24	-29 ≤ h ≤ 32	-14 ≤ h ≤ 14
	-28 ≤ k ≤ 28	-24 ≤ k ≤ 24	-17 ≤ k ≤ 17
	-17 ≤ l ≤ 18	-20 ≤ l ≤ 20	-28 ≤ l ≤ 28
Reflections collected	34711	30337	40100
Independent reflections	5340	8279	15247
R_{int}	4859	0.0449	0.0684
Reflections with $F_0>4\sigma(F_0)$	0.0433	7724	10775
μ / mm^{-1}	1.948	2.337	2.470
Number of parameters	349	475	932
Transm min/max	0.5950/0.8078	0.6517/0.7340	0.6356/0.7561
*R*1 ($F_0>4\sigma(F_0)$)	0.0299	0.0522	0.0573
*R*1 (all data)	0.0348	0.0604	0.0864
*wR*2 (all data)	0.863	0.1415	0.1548
ΔF /e ·Å^{-3}	0.611/-0.813	0.834/-1.119	0.920/-1.266
GOF	1.057	1.184	1.021


a)
simulated
experimental
Intensity / a.u.
10
15
20
25
30
35
40
45
2 θ / °
b)
simulated
experimental
Intensity / a.u.
5
10
15
20
25
30
35
40
45
2 θ / °



Figures S2a-d. Experimental (black) and simulated X-ray powder patterns (red) of compounds **I**-**III** (a-c) and experimental XRDP of **IV** (d).

Table S2. Results of bond valence sum analysis. In the sites of mixed occupancy (Ti(9)/Nb(9) and Ti(10)/Nb(10)), the atom with a site occupancy of 75% is highlighted in bold.

BVS for **I**					
Nb(1)	5.09	Ti(1)	4.04	Ni(1)	2.25
Nb(2)	5.12			Ni(2)	2.21
BVS for **II**					
Nb(1)	5.15	Ti(1)/Nb(5)	4.52	Ni(1)	2.41
Nb(2)	5.13			Ni(2)	2.41
Nb(3)	5.12				
Nb(4)	5.07				
BVS for **III**					
Nb(1)	5.09	Ti(9)/**Nb(9)**	4.79	Ni(1)	2.42
Nb(2)	5.11	**Ti(10)**/Nb(10)	4.27	Ni(2)	2.38
Nb(3)	5.12			Ni(3)	2.37
Nb(4)	5.11			Ni(4)	2.36
Nb(5)	5.12				
Nb(6)	5.13				
Nb(7)	5.07				
Nb(8)	5.07				

Table S3. Nb-O bond lengths in the titanoniobate unit in **I** sorted by type of bridging mode.

Bond type	Atoms	Bond length /Å	Bond type	Atoms	Bond length /Å
Nb=O_t	Nb(1)-O(1)	1.752(2)		Nb(2)-O(8)#2	2.0852(17)
	Nb(2)-O(9)	1.768(2)	Nb-μ_6-O	Nb(1)-O(7)#2	2.4305(19)
Nb-μ_2-O	Nb(1)-O(4)	1.9888(14)		Nb(2)-O(7)#2	2.3829(3)
	Nb(1)-O(2)	1.995(2)		O(7)-Nb(2)#2	2.3829(3)
	Nb(1)-O(3)#1	2.005(2)		O(7)-Nb(2)#3	2.3829(3)
	Nb(1)-O(6)	2.0213(19)		O(7)-Nb(1)#2	2.4305(18)
	Nb(2)-O(3)	1.924(2)		O(7)-Nb(1)#3	2.4305(18)
	Nb(2)-O(2)	1.927(2)	Ti-μ_2-O	Ti(1)-O(6)#3	1.8124(19)
	O(3)-Nb(1)#1	2.005(2)		Ti(1)-O(6)	1.812(2)
	O(4)-Nb(1)#1	1.9888(14)	Ti-μ_3-O	Ti(1)-O(8)	1.962(3)
Nb-μ_3-O	O(8)-Nb(2)#2	2.0850(17)		Ti(1)-O(5)	1.983(3)
	O(8)-Nb(2)#1	2.0850(17)	Ti-μ_6-O	Ti(1)-O(7)	2.1889(17)
	O(5)-Nb(2)#3	2.0787(17)		Ti(1)-O(7)#2	2.1889(17)
	Nb(2)-O(5)	2.0787(17)		O(7)-Ti(1)#2	2.1889(17)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+2 #2 -x+1,-y+1,-z+2 #3 x,-y+1,z.

Table S4. Bond angles / ° in the titanoniobate unit in **I**.

O(1)-Nb(1)-O(4)	104.52(10)	O(2)-Nb(2)-O(8)#2	153.39(10)
O(1)-Nb(1)-O(2)	103.59(9)	O(5)-Nb(2)-O(8)#2	74.86(9)
O(4)-Nb(1)-O(2)	87.26(6)	O(9)-Nb(2)-O(7)#2	171.10(9)
O(1)-Nb(1)-O(3)#1	101.91(9)	O(3)-Nb(2)-O(7)#2	79.71(7)
O(4)-Nb(1)-O(3)#1	88.51(6)	O(2)-Nb(2)-O(7)#2	79.84(7)
O(2)-Nb(1)-O(3)#1	154.40(8)	O(5)-Nb(2)-O(7)#2	74.53(9)
O(1)-Nb(1)-O(6)	102.69(9)	O(8)#2-Nb(2)-O(7)#2	74.74(9)
O(4)-Nb(1)-O(6)	152.78(9)	O(6)#3-Ti(1)-O(6)	105.62(13)
O(2)-Nb(1)-O(6)	86.35(8)	O(6)#3-Ti(1)-O(8)	97.99(8)
O(3)#1-Nb(1)-O(6)	85.95(8)	O(6)-Ti(1)-O(8)	97.99(8)
O(1)-Nb(1)-O(7)#2	178.15(8)	O(6)#3-Ti(1)-O(5)	95.80(8)
O(4)-Nb(1)-O(7)#2	77.03(8)	O(6)-Ti(1)-O(5)	95.80(8)
O(2)-Nb(1)-O(7)#2	77.41(6)	O(8)-Ti(1)-O(5)	157.08(12)
O(3)#1-Nb(1)-O(7)#2	77.04(6)	O(6)#3-Ti(1)-O(7)	86.38(8)
O(6)-Nb(1)-O(7)#2	75.76(7)	O(6)-Ti(1)-O(7)	167.87(8)
O(9)-Nb(2)-O(3)	107.30(10)	O(8)-Ti(1)-O(7)	81.76(6)
O(9)-Nb(2)-O(2)	104.69(9)	O(5)-Ti(1)-O(7)	80.93(6)
O(3)-Nb(2)-O(2)	94.01(9)	O(6)#3-Ti(1)-O(7)#2	167.86(9)
O(9)-Nb(2)-O(5)	97.54(10)	O(6)-Ti(1)-O(7)#2	86.39(8)
O(3)-Nb(2)-O(5)	152.43(10)	O(8)-Ti(1)-O(7)#2	81.76(6)
O(2)-Nb(2)-O(5)	90.99(8)	O(5)-Ti(1)-O(7)#2	80.93(6)
O(9)-Nb(2)-O(8)#2	99.51(10)	O(7)-Ti(1)-O(7)# 2	81.56(10)
O(3)-Nb(2)-O(8)#2	89.15(8)	O(6)#3-Ti(1)-O(6)	105.62(13)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+2; #2 -x+1,-y+1,-z+2; #3 x,-y+1,z

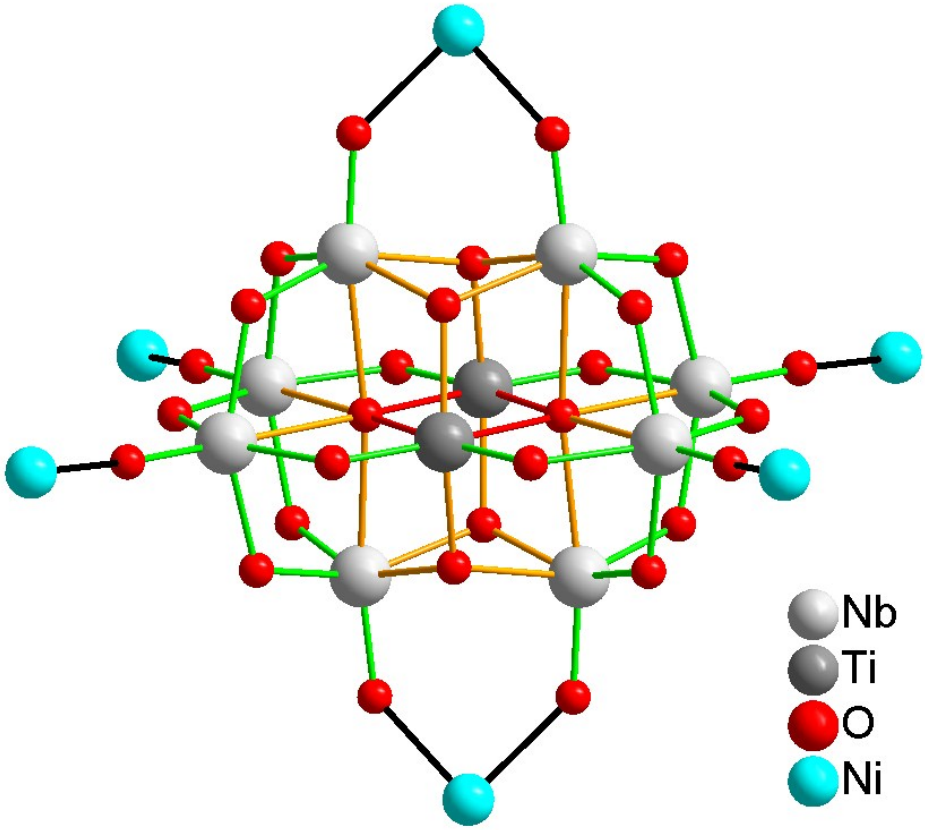


Figure S3. View on the anionic cluster in compound **I**. The bond lengths were compared to known $[Ti_2Nb_8O_{28}]^{8-}$ containing compounds[1][2] and colored as follows: green: good agreement; red: longer bonds; light orange: shorter bonds than reported in literature.

Table. S5. M-O bond lengths (M=Ti/Nb) / Å in title compound sorted by number of bridging atoms and comparison to the bond lengths in the two known dititanioniobates[1][2]. Color code: green: good agreement; red: longer bonds; light orange: shorter bonds than literature-known compounds.

	$[Ni(cyclam)]_4$ $[Ti_2Nb_8O_{28}]\cdot 22H_2O$	$[Cu(en)_2(H_2O)_2]_3$ $[Cu(en)_2][$ $[Ti_2Nb_8O_{28}]\cdot$ $8H_2O$	$Na_8[Ti_2Nb_8O_{28}]\cdot$ $34H_2O$
$Nb{=}O_t$	**1.752(2)-1.768(2)**	1.750(4)-1.764(4)	1.759(2)-1.765(2)
$Nb\text{-}\mu_2\text{-}O$	**1.924(2)-2.0213(19)**	1.919(4)-2.026(4)	1.921(2)-2.032(2)
$Nb\text{-}\mu_3\text{-}O$	**2.0787(17)-2.0850(17**	2.091(4)-2.098(4)	2.099(2)-2.104(2)
$Nb\text{-}\mu_6\text{-}O$	**2.3829(3)-2.4305(18)**	2.415(4)-2.501(4)	2.409(2)-2.481(2)
$Ti\text{-}\mu_2\text{-}O$	**1.812(2)**	1.811(4)-1.833(4)	1.817(2)-1.824(2)
$Ti\text{-}\mu_3\text{-}O$	**1.963(3)-1.983(3)**	1.990(4)-2.011(4)	1.999(2)-2.001(2)
$Ti\text{-}\mu_6\text{-}O$	**2.1889(17)**	2.134(4)-2.153(4)	2.150(2)-2.167(2)

Table S6. Bond lengths / Å and angles / ° for the coordination environment around Ni^{2+} in **I**.

Ni(1)-N(1)	2.062(3)	Ni(2)-N(12)	2.058(7)
Ni(1)-N(1)#4	2.062(3)	Ni(2)-N(13)	2.080(5)
Ni(1)-N(2)	2.073(3)	Ni(2)-N(11)	2.105(5)
Ni(1)-N(2)#4	2.073(3)	Ni(2)-O(9)#3	2.111(2)
Ni(1)-O(1)#4	2.087(2)	Ni(2)-N(14)	2.138(6)
N(1)-Ni(1)-N(1)#4	180.0	N(12)-Ni(2)-N(13)	93.9(4)
N(1)-Ni(1)-N(2)	85.81(12)	N(12)-Ni(2)-N(11)	83.7(3)
N(1)#4-Ni(1)-N(2)	94.19(12)	N(13)-Ni(2)-N(11)	174.8(2)
N(1)-Ni(1)-N(2)#4	94.19(12)	N(12)-Ni(2)-O(9)	87.2(2)
N(1)#4-Ni(1)-N(2)#4	85.81(12)	N(13)-Ni(2)-O(9)	88.0(3)
N(2)-Ni(1)-N(2)#4	180.00(11)	N(11)-Ni(2)-O(9)	96.4(2)
N(1)-Ni(1)-O(1)	89.82(10)	N(12)-Ni(2)-O(9)#3	168.8(2)
N(1)#4-Ni(1)-O(1)	90.18(10)	N(13)-Ni(2)-O(9)#3	95.0(3)
N(2)-Ni(1)-O(1)	91.27(9)	N(11)-Ni(2)-O(9)#3	87.9(2)
N(2)#4-Ni(1)-O(1)	88.73(9)	O(9)-Ni(2)-O(9)#3	86.37(12)
N(1)-Ni(1)-O(1)#4	90.18(10)	N(12)-Ni(2)-N(14)	99.3(2)
N(1)#4-Ni(1)-O(1)#4	89.83(10)	N(13)-Ni(2)-N(14)	83.9(4)
N(2)-Ni(1)-O(1)#4	88.73(9)	N(11)-Ni(2)-N(14)	92.0(3)
N(2)#4-Ni(1)-O(1)#4	91.27(9)	O(9)-Ni(2)-N(14)	169.9(2)
O(1)-Ni(1)-O(1)#4	180.0	O(9)#3-Ni(2)-N(14)	88.32(19)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+2; #2 -x+1,-y+1,-z+2; #3 x,-y+1,z ; #4 -x+1/2,-y+1/2,-z+2.

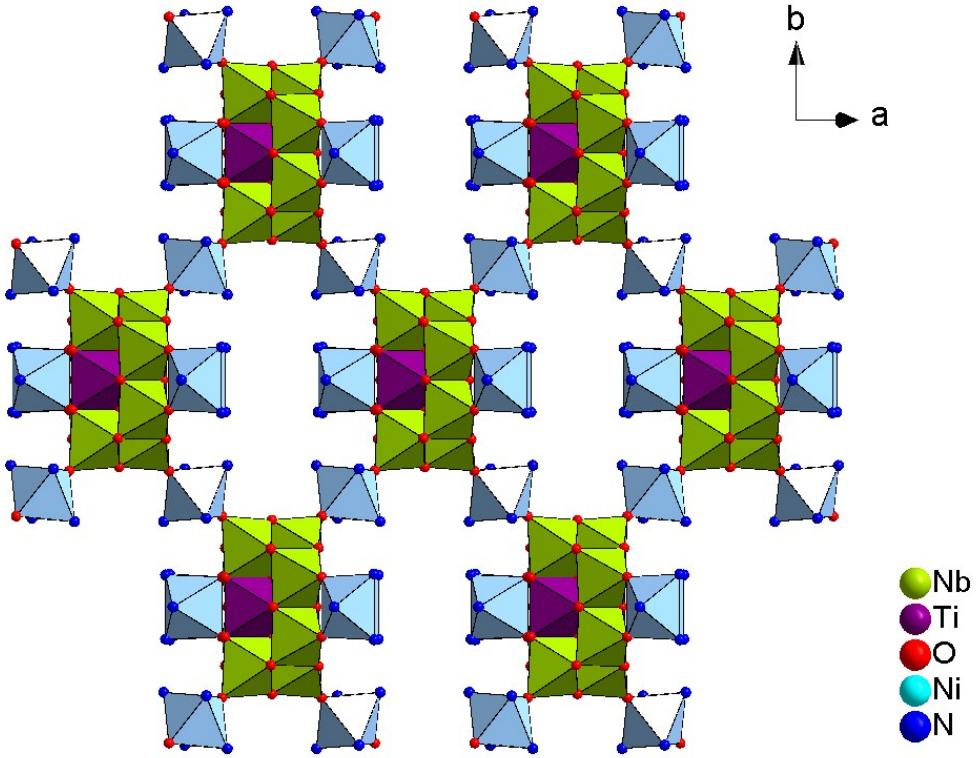
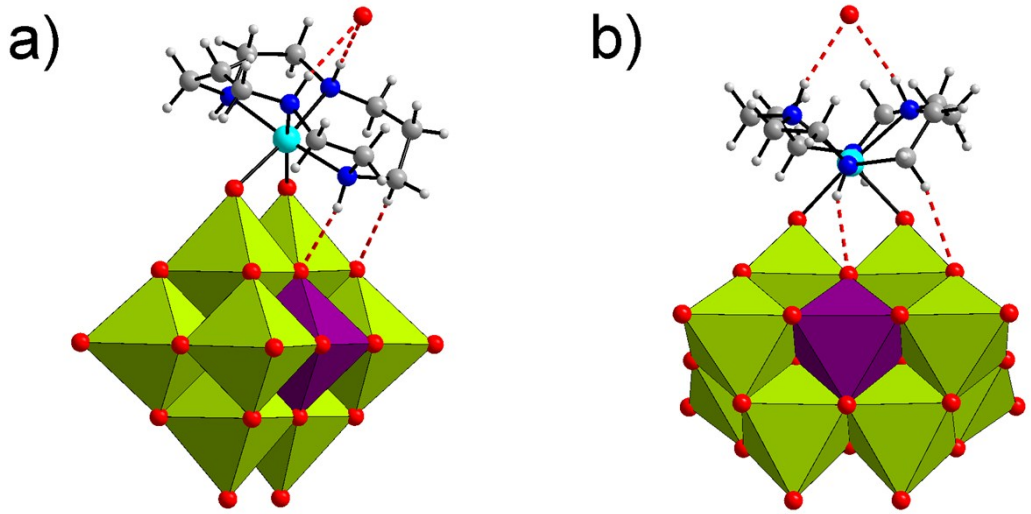


Figure S4. View on the layered structure of $[Ni(cyclam)_4][Ti_2Nb_8O_{28}] \cdot 22H_2O$ (**I**) along [001]; green polyhedra: NbO_6; violet polyhedra: TiO_6; blue polyhedra: NiN_4O_2.

Table S7. Geometrical parameters of hydrogen bonds in **I**.

D-H···A	d(D-H)	d(H···A)	d(D···A)	>(DHA)
N-H…O bonding interactions between cyclam molecules and water or cluster O atoms				
N(2)-H(2)...O(13)#5	1.00	2.21	3.147(4)	155.6
N(11)-H(11)...O(5)	1.00	2.07	2.953(5)	146.3
N(12)-H(12)...O(16)	1.00	2.16	3.114(7)	167.3
N(14)-H(14)...O(16)	1.00	2.16	3.122(7)	161.3
C-H…O bonding interactions between cyclam molecules and cluster O atoms				
C(2)-H(2B)...O(6)	0.99	2.58	3.553(4)	169.0
C(5)-H(5B)...O(1)	0.99	2.65	3.160(4)	112.5
C(13)-H13(B)…O(9)	0.99	2.58	3.093(7)	112.3
C(20)-H(20A)...O(2)#3	0.96	2.43	3.391(7)	163.8

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+2 #2 -x+1,-y+1,-z+2 #3 x,-y+1,z #4 -x+1/2,-y+1/2,-z+2 #5 x-1/2,-y+1/2,z



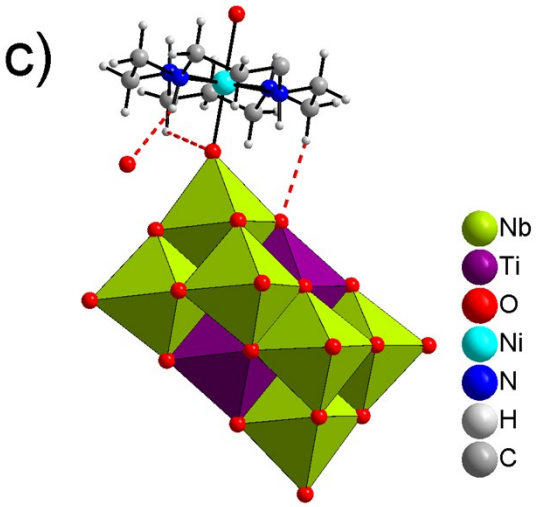


Figure S5a-c. Representation on the H-bonding interactions (dashed lines) in compound **I** involving the *cis*- and the *trans*-[Ni(cyclam)]$^{2+}$ (bottom) molecules in **I**. Only one orientation of the disordered ligand is shown. Green polyhedra: NbO_6, violet polyhedra: TiO_6.

Table S8. O – O distances in water clusters for compounds **I**-**III**.

atom 1	atom 2	distance / Å
compound I		
O(15)	O(16)	2.778
O(12)	O(13)	2.802
O(14)	O(18)	2.828
O(17)	O(14)	2.840
O(11)	O(12)	2.856
O(12)	O(17)	2.875
O(11)	O(12)	2.894
O(14)	O(16)	2.904
Average: 2.847		
compound II		
O(24)	O(29)	2.730
O(24)	O(30)	2.736
O(23)	O(26)	2.738
O(25)	O(26)	2.753
O(22)	O(25)	2.770
O(21)	O(24)	2.778
O(28)	O(28)	2.787
O(21)	O(25)	2.822
O(22)	O(24)	2.824
O(22)	O(28)	2.837
O(27)	O(27)	2.859
O(24)	O(30)	2.873
O(23)	O(27)	2.873
O(22)	O(23)	2.891
O(23)	O(23)	2.910
Average: 2.812		
compound II		
O(36)	O(42)	2.698
O(42)	O(35)	2.725
O(7)	O(41)	2.725
O(38)	O(6)	2.732
O(43)	O(44)	2.751
O(35)	O(3)	2.765
O(36)	O(40)	2.769
O(37)	O(4)	2.769
O(40)	O(43)	2.790
O(41)	O(39)	2.802
O(8)	O(43)	2.806
O(39)	O(3)	2.811
O(8)	O(40)	2.840
O(41)	O(38)	2.847
O(42)	O(41)	2.871
O(37)	O(32)	2.948
Average: 2.791		

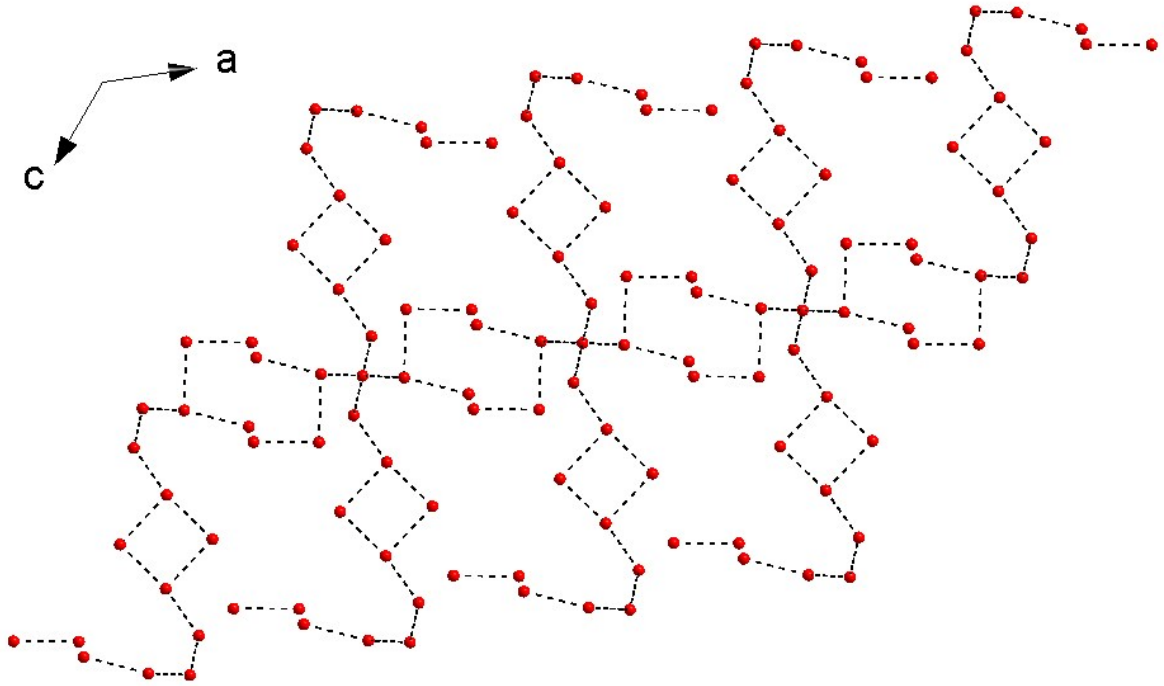


Figure S6. View on the arrangement of water O atoms in the water cluster in **I** along b axis. O – O distances up to 3.04 Å shown in dashed lines.

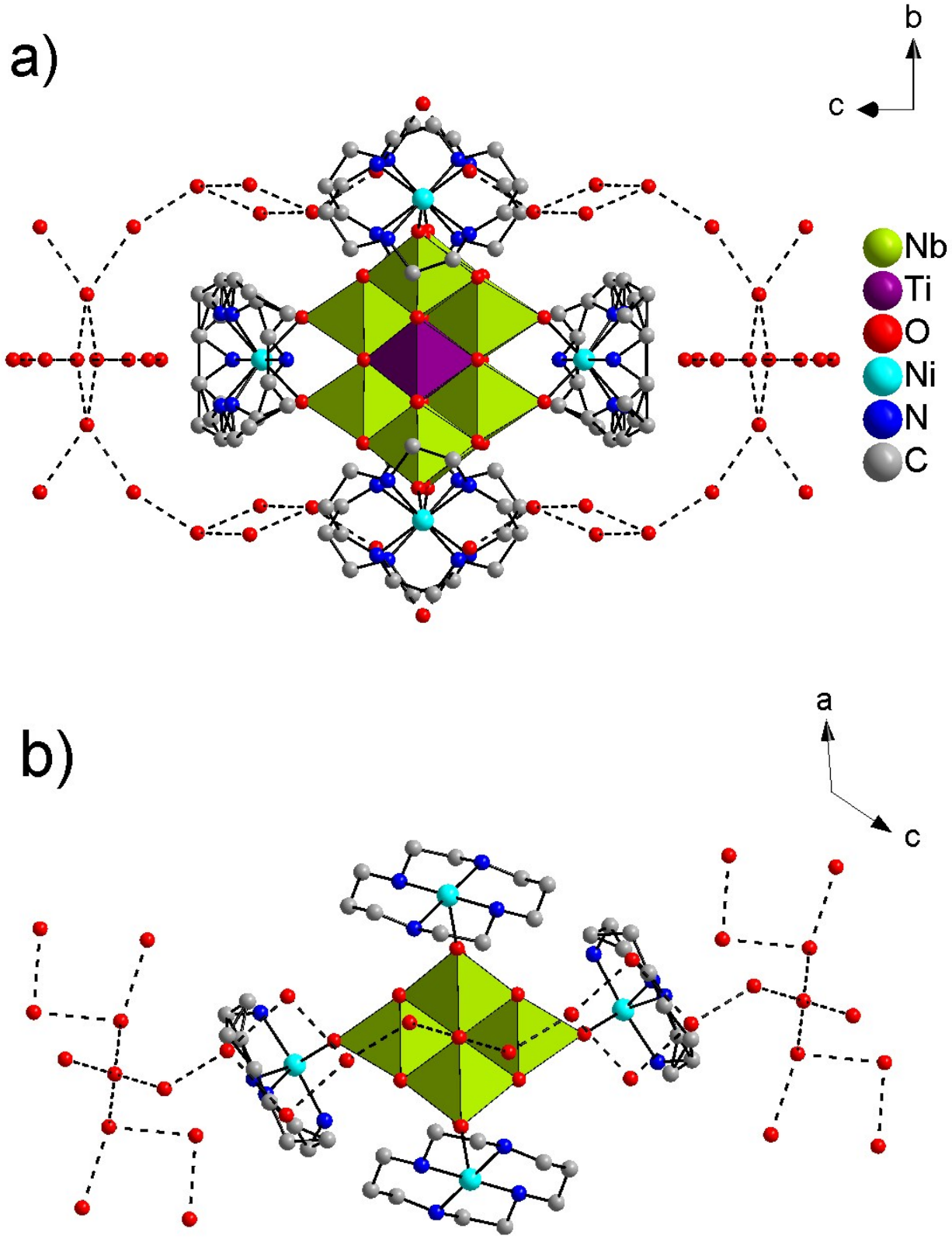


Figure S7a-b. Arrangement of the differently coordinated $[Ni(cyclam)]^{2+}$ molecules in **I** with respect to the water cluster. O – O distances up to 3.04 Å shown in dashed lines. Green polyhedra: NbO_6, violet polyhedra: TiO_6. H atoms omitted for clarity.

Table S9. Nb-O bond lengths / Å in the titanoniobate unit in **II** sorted by type of bridging mode.

Bond type	Atoms	Bond length /Å	Bond type	Atoms	Bond length /Å
Nb=O_t	Nb(1)-O(1)	1.741(6)		Nb(4)-O(10) #1	2.106(4)
	Nb(2)-O(11)	1.756(4)		O(9)-Nb(2)#1	2.102(4)
	Nb(3)-O(12)	1.743(5)		O(10)-Nb(4)#1	2.106(4)
	Nb(4)-O(13)	1.763(4)	Nb-μ_6-O	Nb(1)-O(6) #1	2.486(4)
Nb-μ_2-O	Nb(1)-O(2)	1.995(4)		Nb(2)-O(6)#1	2.390(4)
	Nb(1)-O(3)	1.953(4)		Nb(3)-O(6)#1	2.496(4)
	Nb(1)-O(5)	2.065(4)		O(6)-Nb(4)#1	2.399(4)
	Nb(1)-O(4)	1.982(4)		O(6)-Nb(2)#1	2.390(4)
	Nb(2)-O(2)	1.923(4)		O(6)-Nb(1)#1	2.486(4)
	Nb(2)-O(7)	1.905(4)		O(6)-Nb(3)#1	2.493(4)
	Nb(3)-O(3)	1.944(4)		Nb(3)-O(6)#1	2.493(4)
	Nb(3)-O(7)	1.985(4)		Nb(4)-O(6)#1	2.399(4)
	Nb(3)-O(8)	2.012(4)	Ti/Nb-μ_2-O	Ti(1)/Nb(5)-(O14)	1.815(4)
	Nb(3)-O(14)#1	2.068(4)		Ti(1)/Nb(5)-(O5)	1.827(4)
	Nb(4)-O(4)	1.913(4)	Ti/Nb -μ_3-O	Ti(1)/Nb(5)-(O9)	1.999(4)
	Nb(4)-O(8)	1.933(4)		Ti(1)/Nb(5)-(O10)	1.992(4)
	O(14)-Nb(3)#1	2.068(4)	Nb/Ti-μ_6-O	Ti(1)/Nb(5)-(O6)	2.191(4)
Nb-μ_3-O	Nb(2)-O(9)#1	2.102(4)		O(6)- Ti(1)/Nb(5)#1	2.208(4)
	Nb(2)-O(10)	2.116(4)		Ti(1)/Nb(5)-O(6)#1	2.208(4)
	Nb(4)-O(9)	2.098(4)			

Symmetry transformations used to generate equivalent atoms: #1 -x+3/2,-y+3/2,-z+1; #2 -x+2,y,-z+3/2.

Table S10. Comparison of the bond lengths / Å in the anionic units of compounds **II** and **III** with those reported for $(TMA)_7[TiNb_9O_{28}]\cdot 22H_2O$[3].

Bond type	Compound **II**	Compound **III**	$TiNb_9$[3]
Nb=O_t	1.741(6)- 1.763(4)	1.737(5)- 1.768(5)	1.746(4)-1.770(4)
Nb-μ_2-O	1.905(4)- 2.068(4)	1.907(5)- 2.098(5)	1.900(4)-2.078(4)
Nb-μ_3-O	2.098(4)- 2.116(4)	2.074(5)- 2.119(4)	2.086(4)-2.127(4)
Nb-μ_6-O	2.390(4)- 2.496(4)	2.394(4)- 2.520(4)	2.398(4)-2.512(4)
Ti/Nb-μ_2-O	1.815(4)- 1.827(4)	1.808(5)- 1.826(5)	1.809(4)-1.815(4)
Ti/Nb-μ_3-O	1.992(4)- 1.999(4)	1.994(4)- 2.023(4)	2.001(4)-2.028(4)
Ti/Nb-μ_6-O	2.191(4)- 2.208(4)	2.182(5)- 2.228(5)	2.183(4)-2.222(4)

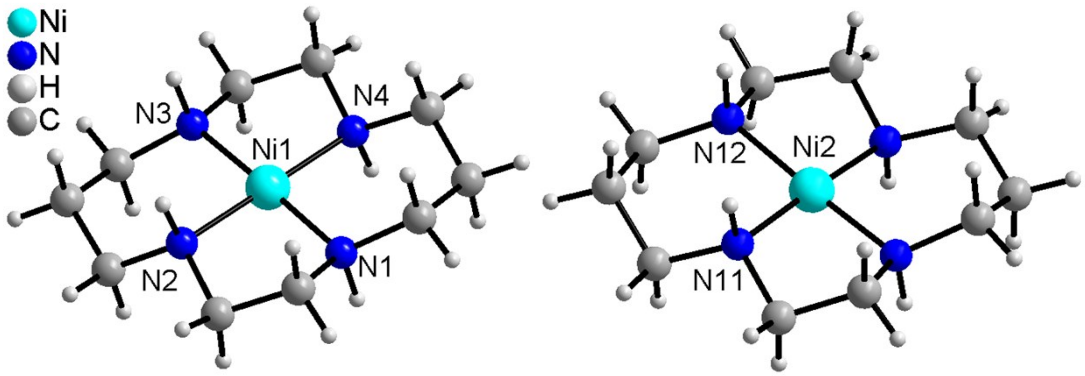


Figure S8. Coordination environment of the $[Ni(cyclam)]^{2+}$ cations in the structure of **II**.

Table S11. Ni-N bond lengths / Å and N-Ni-N bond angles / ° for the $[Ni(cyclam)]^{2+}$ cations in compound **II**.

Ni(1)-N(1)	1.923(6)	Ni(2)-N(11)	1.923(6)
Ni(1)-N(2)	1.941(6)	Ni(2)-N(11)#2	1.923(6)
Ni(1)-N(3)	1.933(6)	Ni(2)-N(12)#2	1.938(5)
Ni(1)-N(4)	1.926(6)	Ni(2)-N(12)	1.938(5)
N(1)-Ni(1)-N(4)	94.1(3)	N(11)#2-Ni(2)-N(11)	86.2(3)
N(1)-Ni(1)-N(3)	178.4(2)	N(11)#2-Ni(2)-N(12)#2	93.5(2)
N(1)-Ni(1)-N(2)	86.0(3)	N(11)-Ni(2)-N(12)#2	176.1(2)
N(4)-Ni(1)-N(2)	179.7(2)	N(11)#2-Ni(2)-N(12)	176.1(2)
N(4)-Ni(1)-N(3)	86.8(3)	N(11)-Ni(2)-N(12)	93.5(2)
N(3)-Ni(1)-N(2)	93.2(3)	N(12)#2-Ni(2)-N(12)	87.1(3)

Symmetry transformations used to generate equivalent atoms: #1 -x+3/2,-y+3/2,-z+1 #2 -x+2,y,-z+3/2.

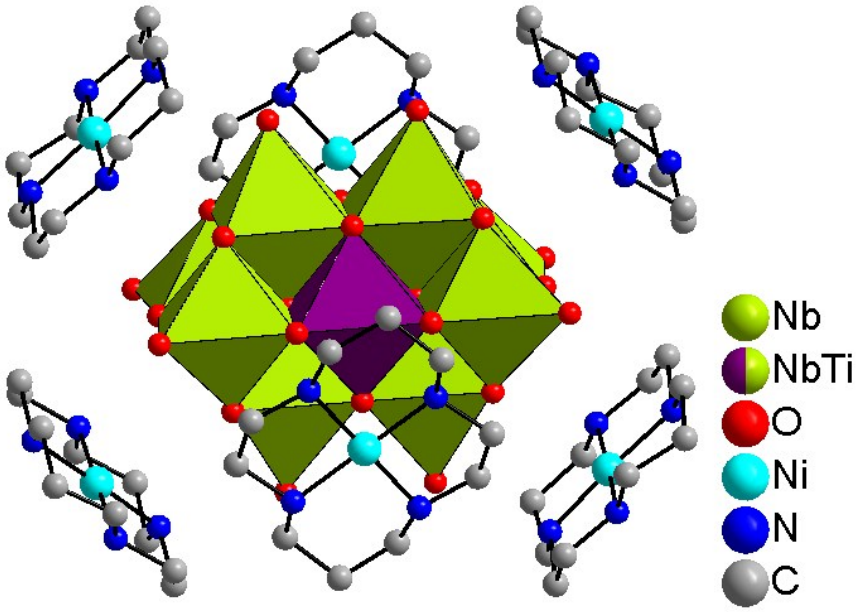


Figure S9. The $[TiNb_9O_{28}]^{7-}$ anion in the structure of **II** surrounded by six $[Ni(cyclam)]^{2+}$ cations. H and K atoms are not displayed. Green polyhedra: NbO_6, violet polyhedra: TiO_6.

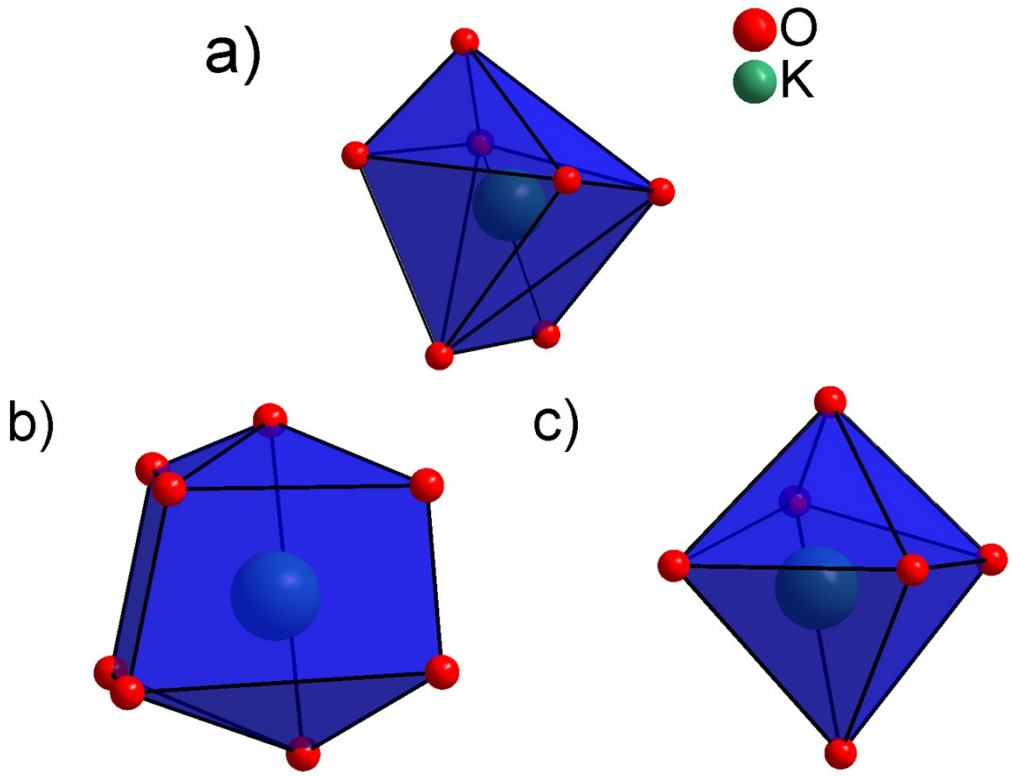


Figure S10a-c. Coordination environment of K^+ cations in the structure of **II** (a) and **III** (b-c) surrounded by water molecules and cluster O atoms.

Table S12. K-O bond lengths / Å in the structure of compounds **II** and **III**.

Compound **II**		Compound **III**			
atoms	distance / Å	atoms	distance / Å	atoms	distance / Å
K(1)-O(11)	2.841(6)	K(1)-O(13)	3.035(6)	K´(1)- O(33)	2.952(16)
K(1)#1-O(13)	2.874(6)	K(1)-O(15)	3.079(6)	K´(1)- O(33)	2.691(16)
K(1)-O(13)#1	2.874(6	K(1)-O(31)	2.697(12)	K´(1)- O(34)	2.831(13)
K(1)-O(24)	2.806(7)	K(1)-O(31)	3.133(13)	K´(1)- O(37)	2.601(7)
K(1)-O(25)	2.796(7)	K(1)-O(32)	3.060(14)	K´(1)- O(39)	3.057(8)
K(1)-O(26)	3.016(9)	K(1)-O(32)	3.104(15)	K´(1)- O(46)	2.815(13)
K(1)-O(29)	3.054(8)	K(1)-O(39)	2.774(8)		
K(1)-O(30)	2.734(12)	K(1)-O(46)	3.052(12)		
Average: 2.874		**Average:** 2.920			

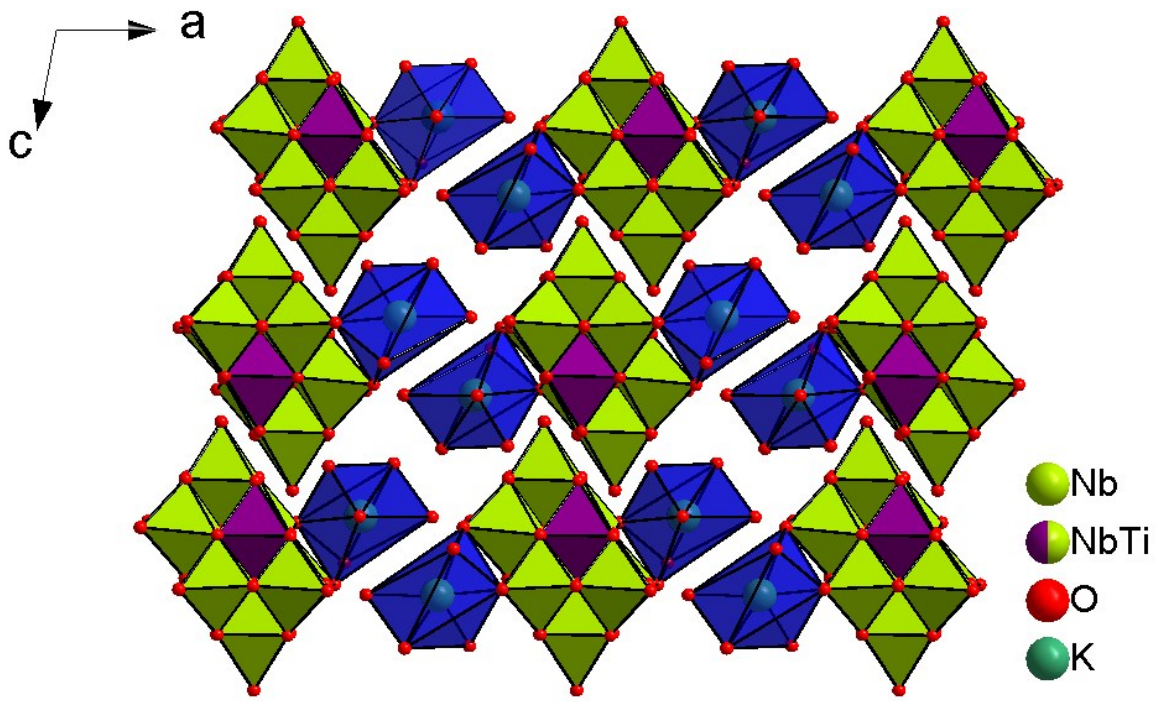


Figure S11. Arrangement of the KO_7 polyhedra and $[TiNb_9O_{28}]^{7-}$ anions in the structure of **II** along [010]. The $[Ni(cyclam)]^{2+}$ cations and water O atoms which are not involved in K-O interactions are omitted. Green: NbO_6, violet: Ti/NbO_6, blue: KO_7 polyhedra.

Table S13. Geometrical parameters of hydrogen bonds in **II**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N-H…O bonding interactions between cyclam molecules and cluster O atoms				
N(1)-H(1)...O(14)	1.00	2.01	2.937(7)	152.9
N(2)-H(2)...O(1)#3	1.00	2.37	3.238(8)	145.1
N(2)-H(2)...O(2)#3	1.00	2.47	3.302(7)	139.9
N(3)-H(3)...O(2)#3	1.00	2.61	3.395(7)	135.9
N(3)-H(3)...O(11)#3	1.00	2.17	3.031(7)	143.1
N(4)-H(4)...O(5)	1.00	1.85	2.837(7)	169.4
N(11)-H(11)...O(13)	1.00	1.84	2.828(7)	170.4
N(12)-H(12)...O(8)	1.00	2.03	2.996(7)	160.6
C-H…O bonding interactions between cyclam molecules and cluster O atoms				
C(1)-H(1B)...O(3)#3	0.99	2.53	3.446(9)	153.5
C(2)-H(2A)...O(12)#1	0.99	2.63	3.454(9)	140.5
C(3)-H(3A)...O(7)#1	0.99	2.65	3.574(9)	156.3
C(6)-H(6A)...O(4)	0.99	2.41	3.373(9)	165.0
C(7)-H(7A)...O(11)#3	0.99	2.45	3.194(9)	131.2
C(8)-H(8B)...O(7)#3	0.99	2.58	3.493(9)	152.9
C(10)-H(10A)...O(12)#3	0.99	2.59	3.507(9)	153.5
C(12)-H(12B)...O(4)#2	0.99	2.62	3.514(8)	150.1
C(14)-H(14A)...O(1)#2	0.99	2.64	3.540(9)	150.5
C(15)-H(15A)...O(3)#2	0.99	2.47	3.421(8)	161.2
C-H…O bonding interactions between cyclam molecules and water O atoms				
C(4)-H(4A)...O(25)#3	0.99	2.59	3.517(11)	155.3
C(5)-H(5B)...O(30)#3	0.99	2.48	3.434(15)	163.1
C(9)-H(9B)...O(23)	0.99	2.64	3.558(10)	153.7
C(11)-H(11A)...O(30)#4	0.99	2.58	3.229(14)	122.7
C(13)-H(13B)...O(22)#5	0.99	2.64	3.595(9)	162.3

Symmetry transformations used to generate equivalent atoms:#1 -x+3/2,-y+3/2,-z+1; #2 -x+2,y,-z+3/2; #3 -x+3/2,y-1/2,-z+3/2; #4 x+1/2,y-1/2,z; #5 x+1/2,-y+3/2,z-1/2.

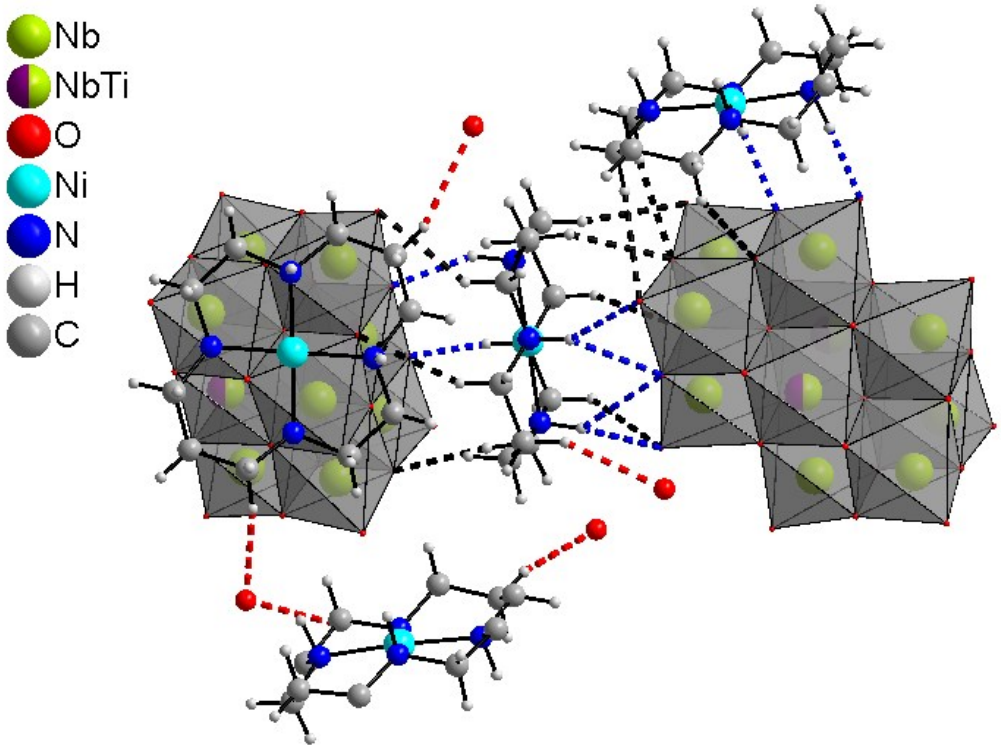


Figure S12. H bonding interactions in the structure of compound **II** shown in dashed lines. Color code: N-H···O(cluster): blue, C-H···O(cluster): black, C-H···O(water): red. Grey polyhedra: Ti/NbO_6 units.

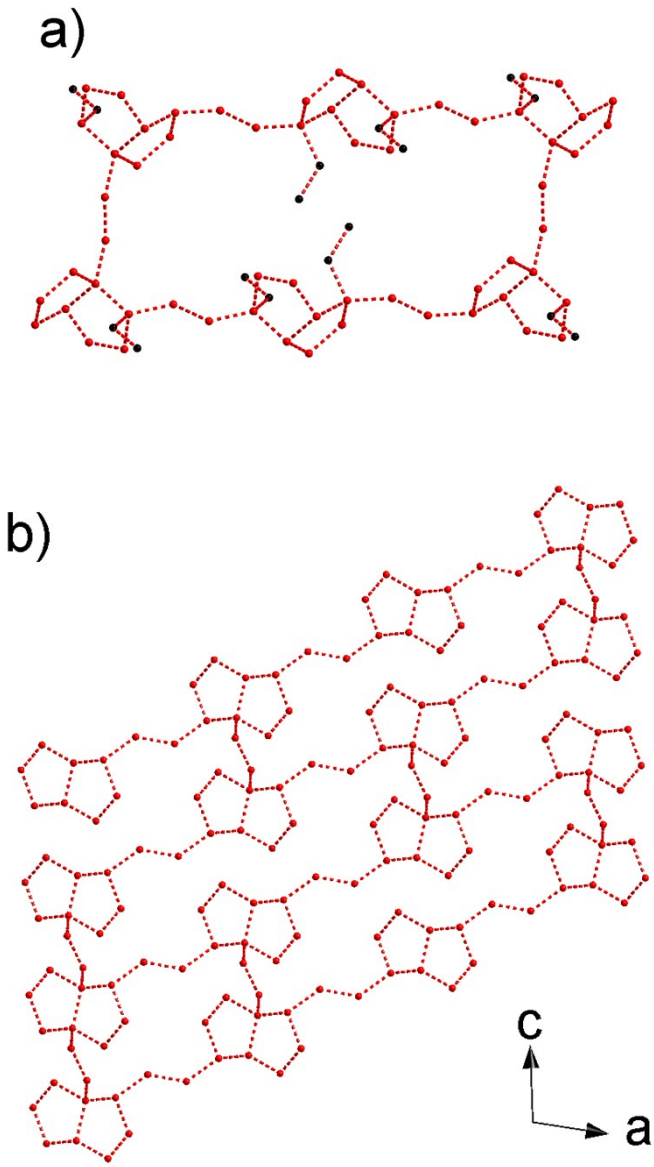


Figure S13a-b. View on the arrangement of water O atoms in **II**. O-O distances below the sum of the van der Waals radii in dashed lines. a) View on the L5(4)30(18) building unit. The isolated fragments consisting of two water molecules (O24,O29) attached to the water cluster are displayed in black and omitted in b) View on the L5(4)30(18) type water cluster along [010].

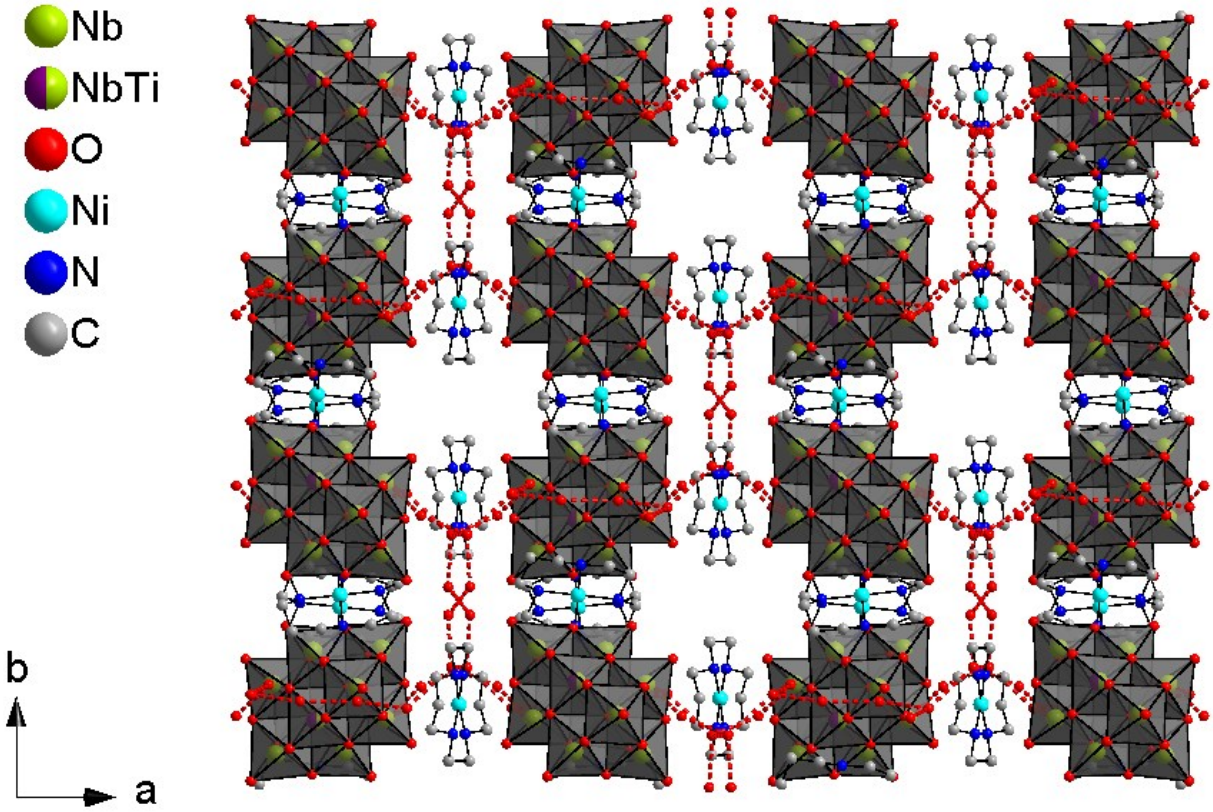


Figure S14. The L5(4)L30(18) water cluster in the structure of **II** (grey polyhedra: Ti/NbO_6), which are connected via two water O atoms along b axis. The water O atoms that do not expand the network (O24+O29), K and H atoms omitted.

Table S14. Comparison of selected bond lengths and angles in compound **II** and **III**.

	Nb=O_t bond lengths / Å	Nb-μ_2-O bond lengths / Å	Nb-μ_3-O bond lengths / Å
II	1.741(6) – 1.763(4)	1.905(4) – 2.068(4)	2.098(4) – 2.116(4)
III	1.737(5) – 1.768(5)	1.907(5) – 2.098(5)	2.074(5) – 2.119(4)
	Nb-μ_6-O bond lengths / Å	Ti/Nb-μ_2-O bond lengths / Å	Ti/Nb-μ_3-O bond lengths / Å
II	2.390(4) -2.496(4)	1.815(4) – 1.827(4)	1.992(4) - 1.999(4)
III	2.394(4) – 2.520(4)	1.808(5) – 1.826(5)	1.994(4) – 2.023(4)
	Ti/Nb-μ_6-O bond lengths / Å	Nb-O-Nb angles / °	Ni-N bond lengths /Å
II	2.191(4) - 2.208(4)	73.6(1) – 178.2(2)	1.923(6) – 1.941(6)
III	2.182(5) – 2.228(5)	73.45(17) – 177.9(2)	1.919(6) – 1.941(6)
	Ti/Nb-O-Ti/Nb angles / °	Ni-N *cis*-angles / °	Ni-N *trans*-angles / °
II	79.37(15) – 166.30(16)	86.0(3) – 93.5(2)	176.1(2) – 179.7(2)
III	80.03(17) – 166.5(2)	86.5(3) – 93.4(3)	177.2(2) – 180.0
	N-H···$O_{cluster}$ / Å	C-H···$O_{cluster}$ / Å	C-H···O_{water} / Å
II	2.828(7) – 3.238(8)	3.194(9) – 3.574(9)	3.23(1) – 3.595(9)
III	2.830(8) – 3.465(7)	3.130(10) – 3.523(11)	3.191(14) – 3.522(10)
	< (NHO) / °	< ($CHO_{cluster}$) / °	< (CHO_{water}) / °
II	143.1 – 170.4	131.2 – 165.0	122.7 – 163.1
III	138.6 – 171.6	137.0 – 178.3	137.0 – 178.3

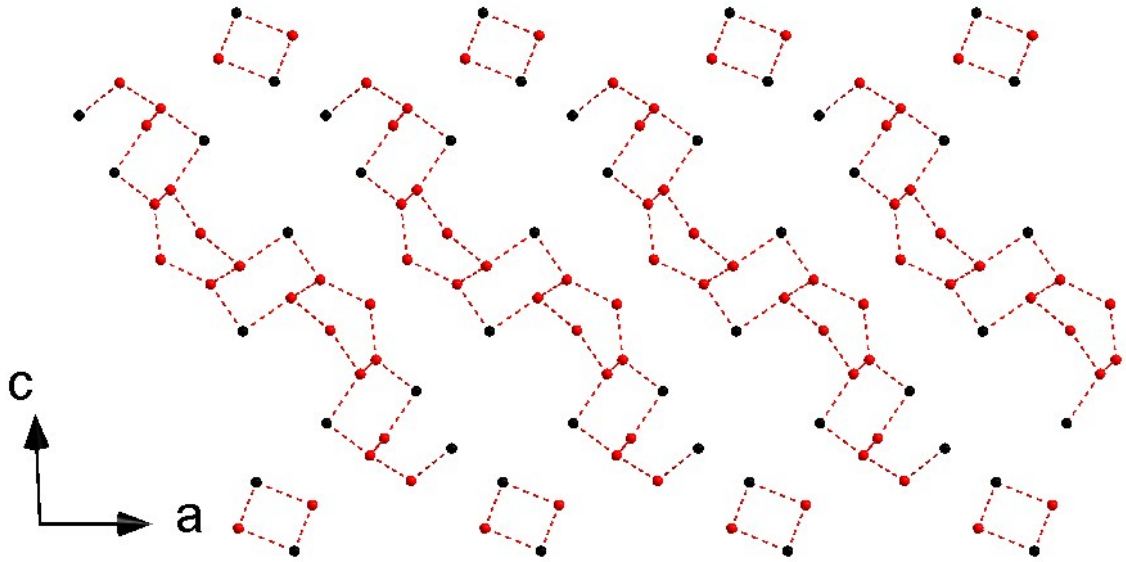


Figure S15. The extended water motif involving water (red) and cluster (black) O atoms in the structure of compound **III.**

Infrared spectroscopy

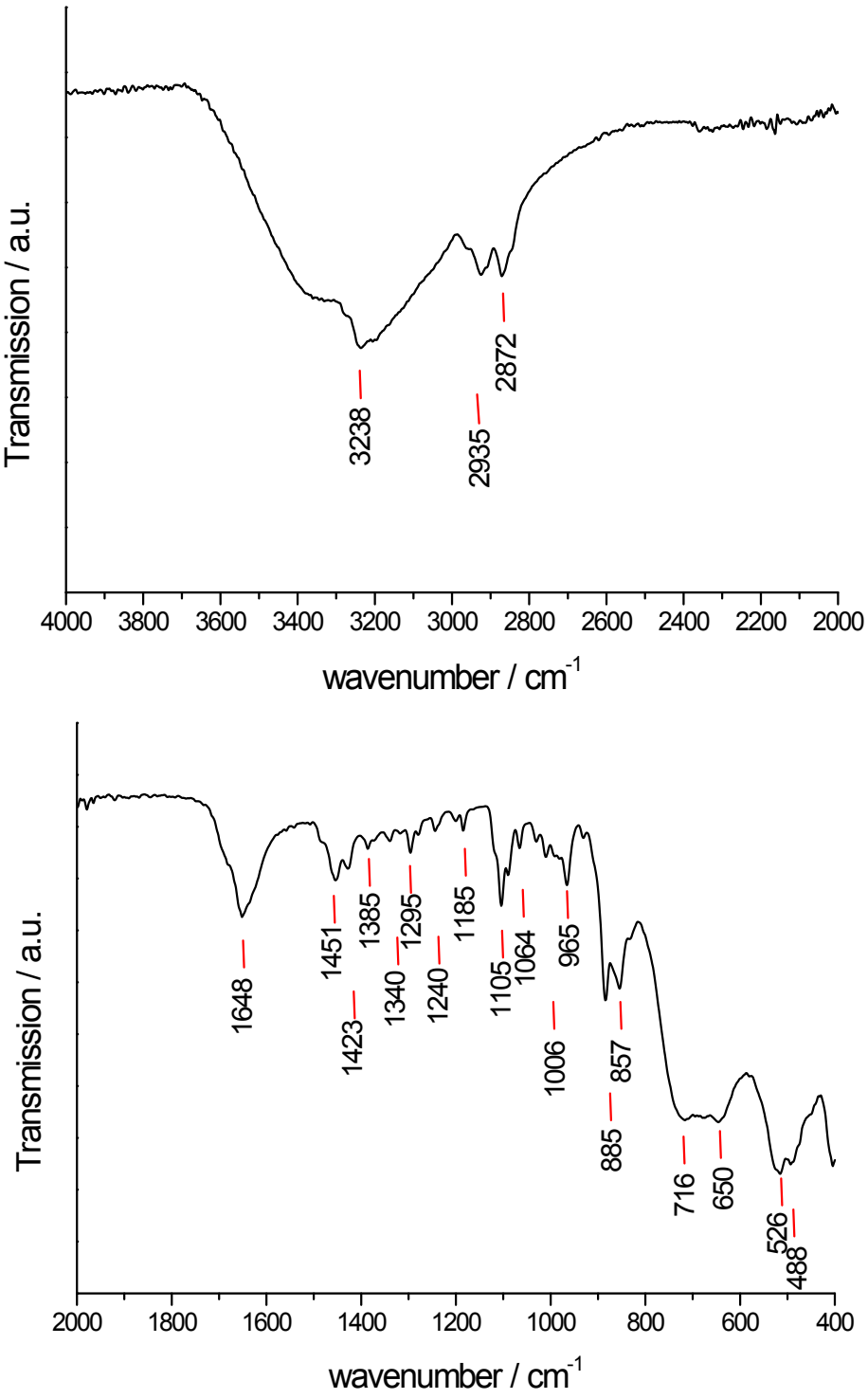


Figure S16. Infrared spectrum of compound **I**.

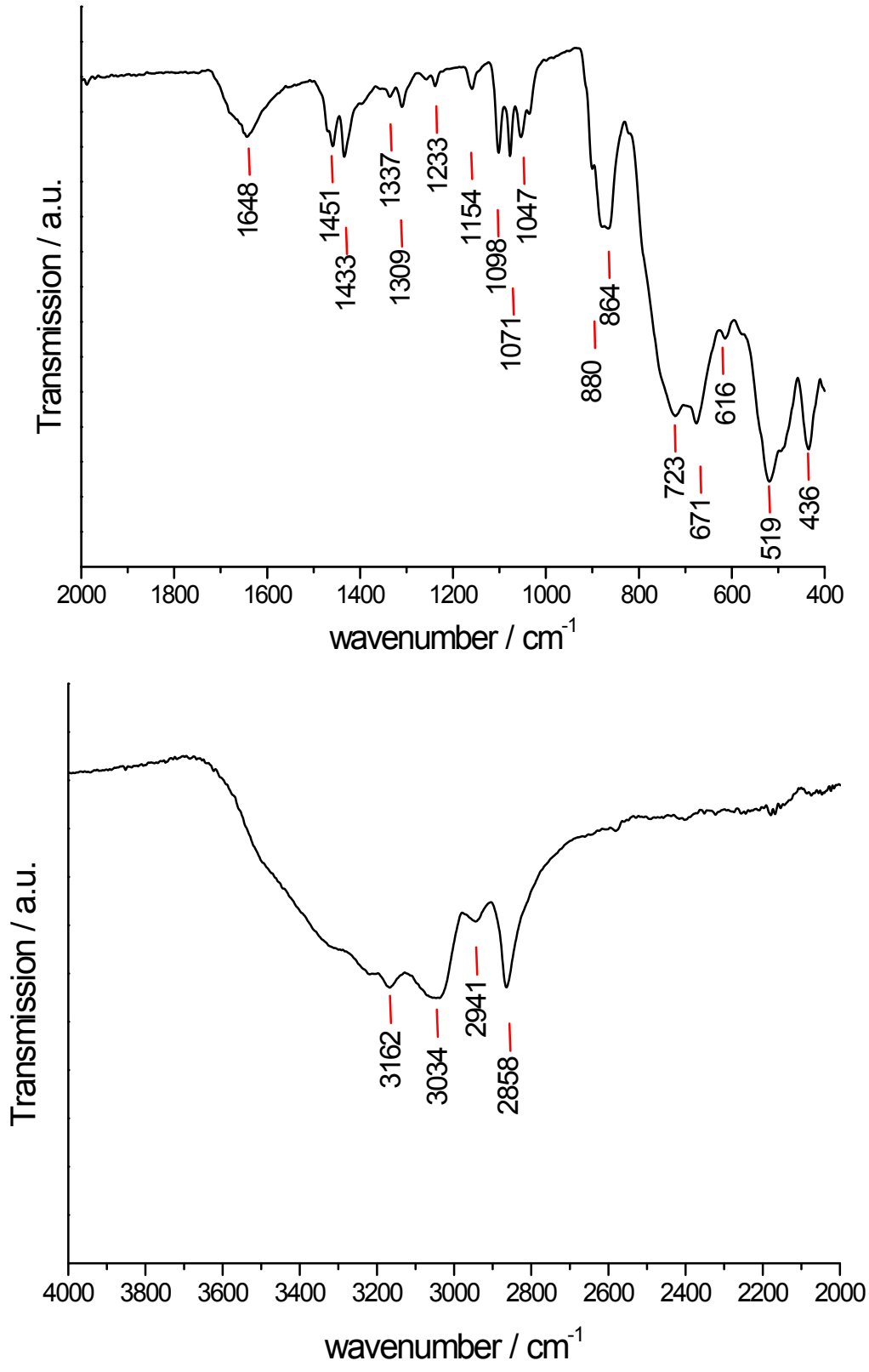


Figure S17. Infrared spectrum of compound **II**.

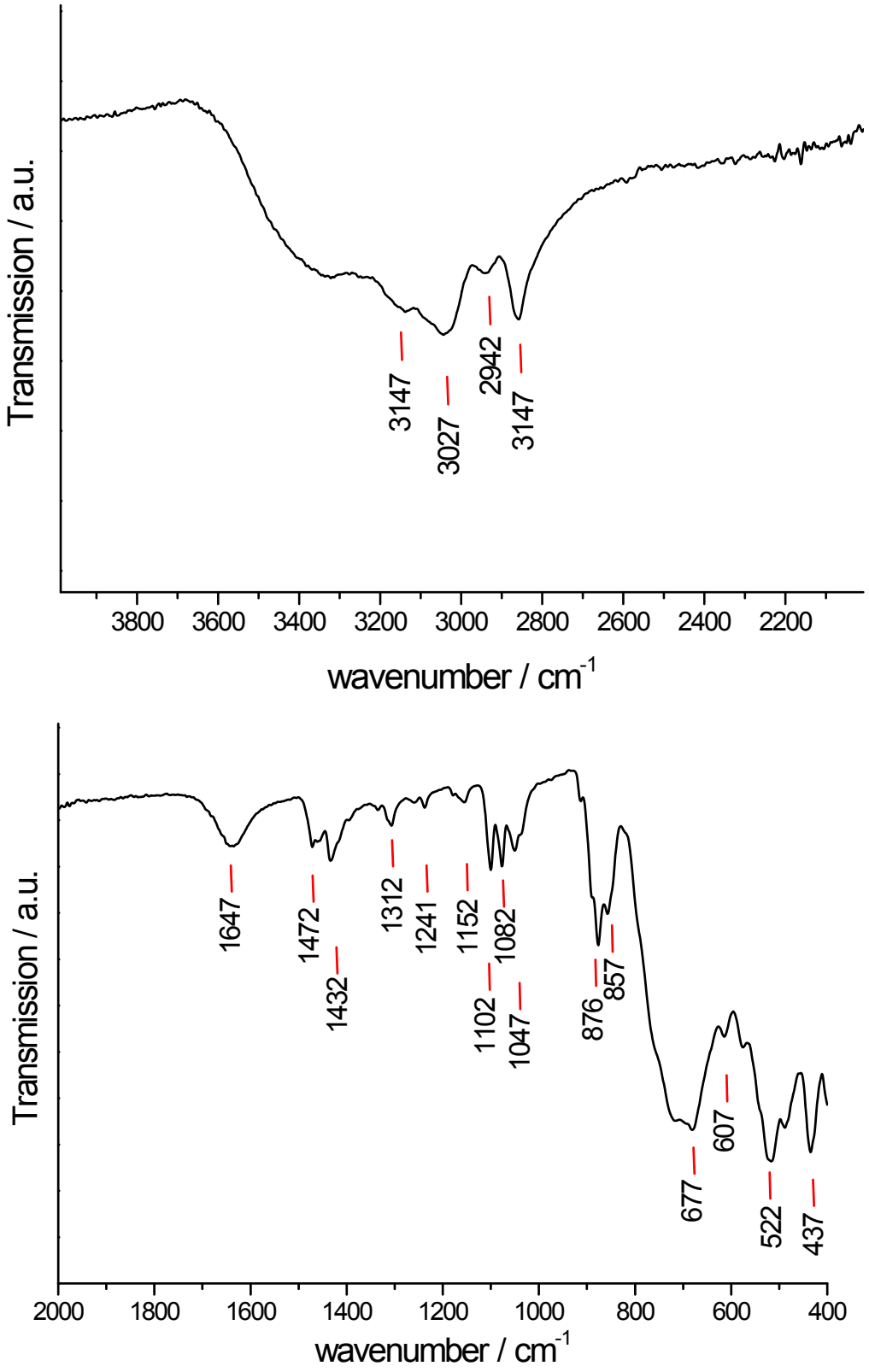


Figure S18. Infrared spectrum of compound **III**.

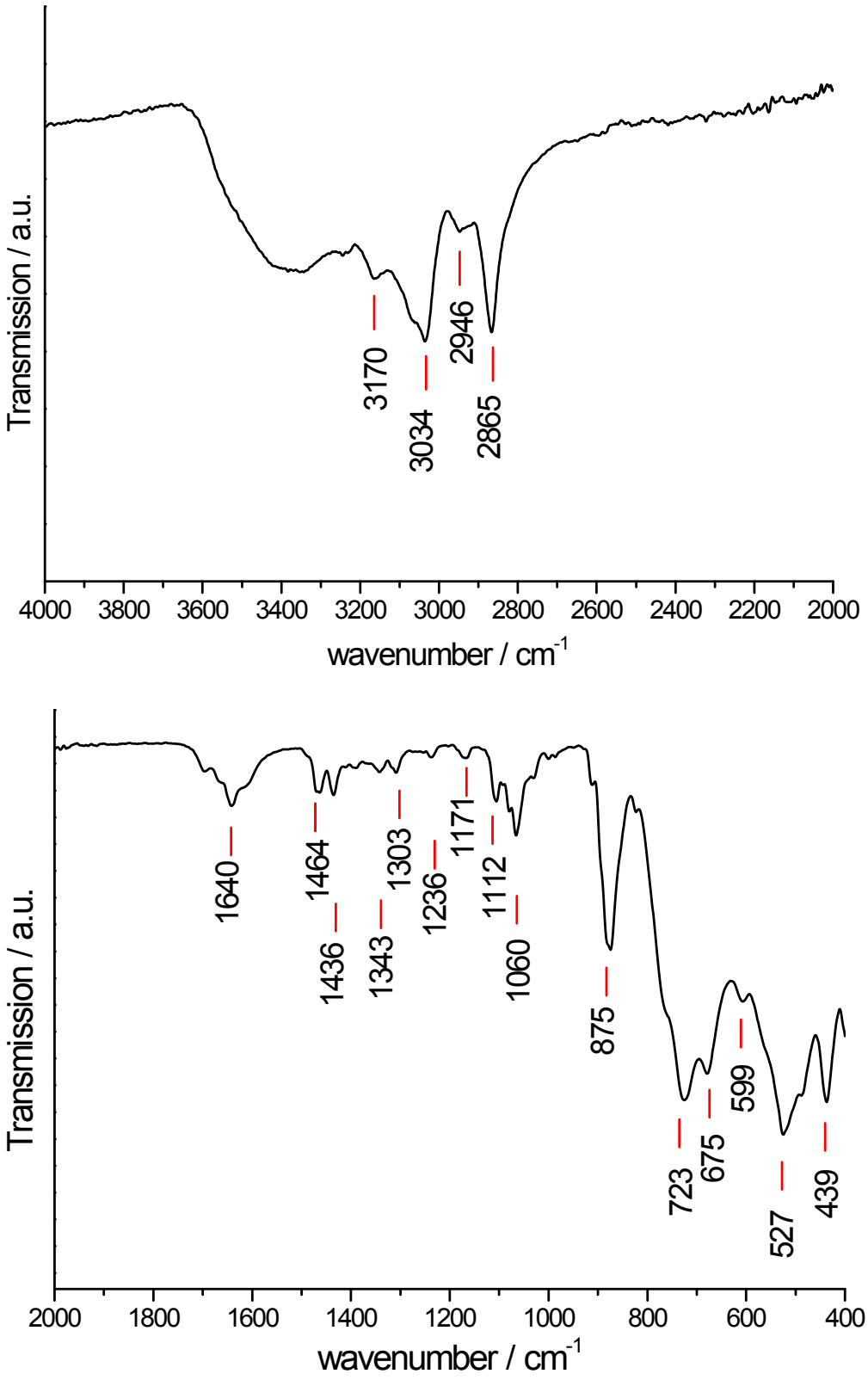


Figure S19. Infrared spectrum of compound **IV**.

Table S15. Assignment of the IR absorptions compared to literature-known compounds[4].

I	**II**	**III**	**IV**	assignment	$[Nb_{10}O_{28}]^{6-}$ [5]	$[Ti_2Nb_8O_{28}]^{8-}$ [2]
3238	3162	3147	3170	ν (N-H)		
	3034	3027	3034	ν (N-H)		
2935	2941	2942	2946	ν (C-H)		
2872	2858	2847	2865	ν (C-H)		
1648	1647	1647	1640	δ (O-H)		
1451	1458	1472	1464	ν (C-C) + ν (C-N)		
1423	1433	1432	1436	ν (C-C) + ν (C-N)		
1385				ν (C-C) + ν (C-N)		
1340	1337		1343	ν (C-C) + ν (C-N)		
1295	1309	1312	1303	ν (C-C) + ν (C-N)		
1240	1233	1241	1236	ν (C-N) + δ (C-H)		
1185	1154	1152	1171	ν (C-N) + δ (C-H)		
1105	1098	1102	1112	ν (C-C) + δ (C-N)		
1064	1071	1082	1060	ν (C-C) + δ (C-N)		
	1047	1047		ν (C-C) + δ (C-N)		
1006				ν (C-C) + δ (C-N)		
965				δ (N-H)/Nb-O_t		975
885	880	876	875	δ (N-H)/ Nb-O_t	886	
857	864	857		Nb-O_t	859	800
716	723		723	Ti/Nb-O-Ti/Nb	746,765	752
650	671	677	675	Ti/Nb-O-Ti/Nb	649	
	616	607	599	Ti/Nb-O-Ti/Nb		
526	519	522	527	macrocycl. def./ Nb-O-Nb	507, 534	524
488				Ti/Nb-O-Ti/Nb		
	436	437	439	Ti/Nb-O-Ti/Nb	434	

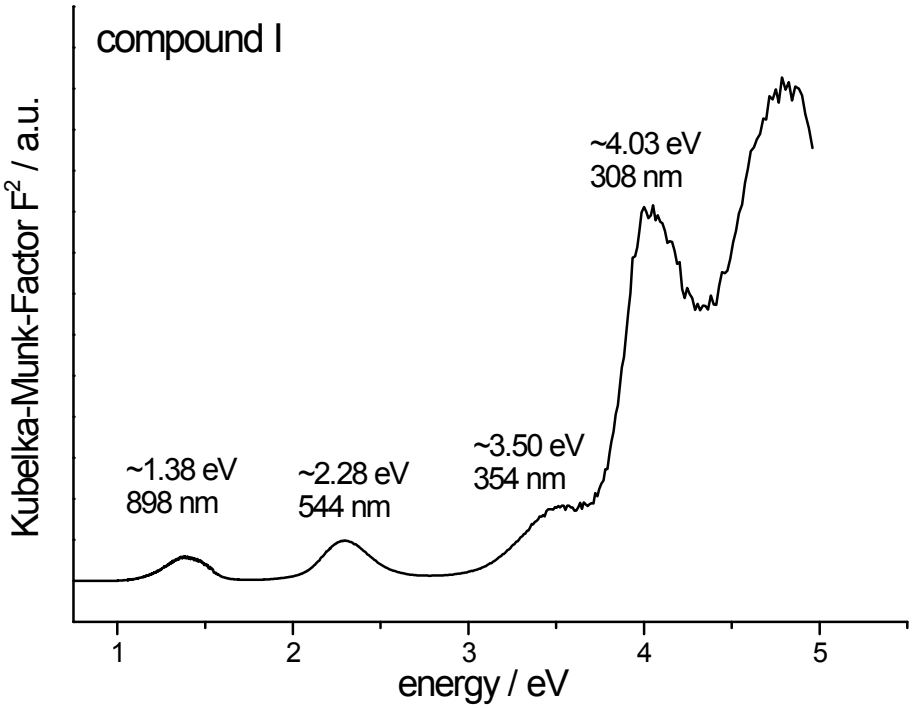


Figure S20. UV/Vis diffuse reflectance spectrum of compound **I**.

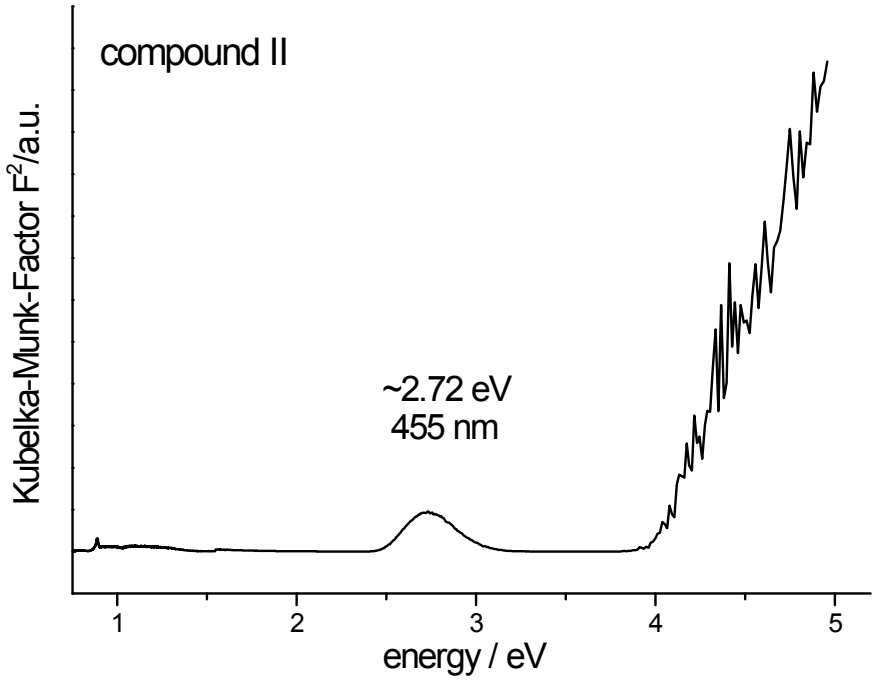


Figure S21. UV/Vis diffuse reflectance spectrum of compound**II**.

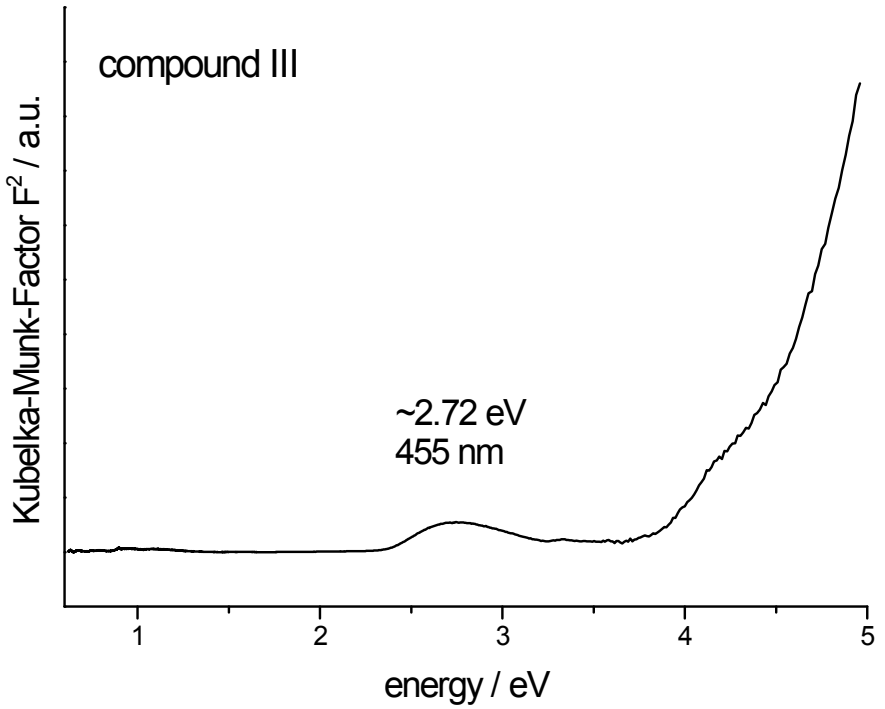


Figure S22. UV/Vis diffuse reflectance spectrum of compound **III**.

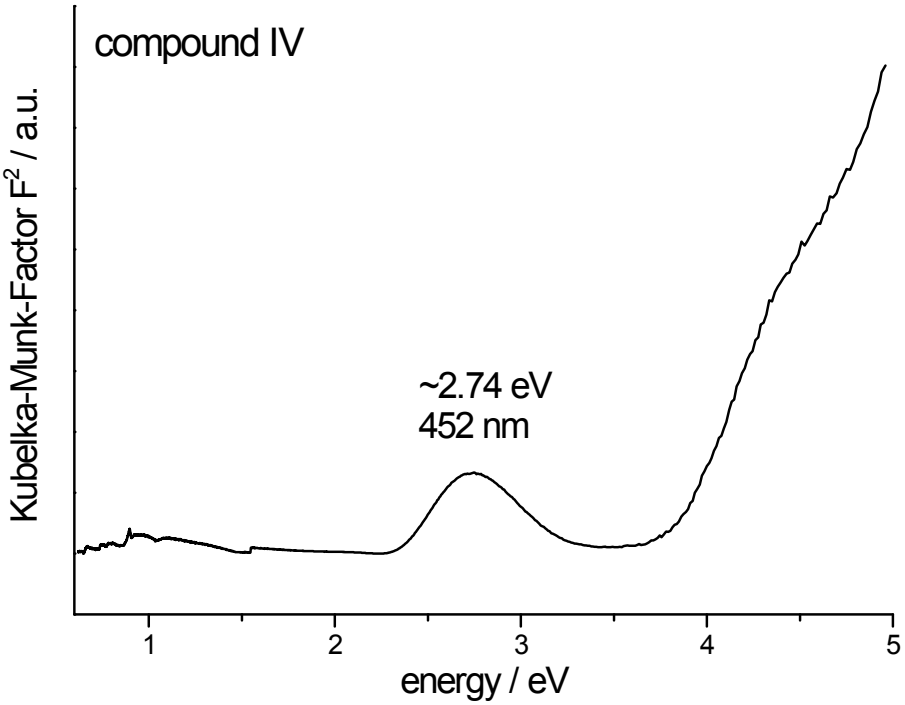


Figure S23. UV/Vis diffuse reflectance spectrum of compound **IV**.

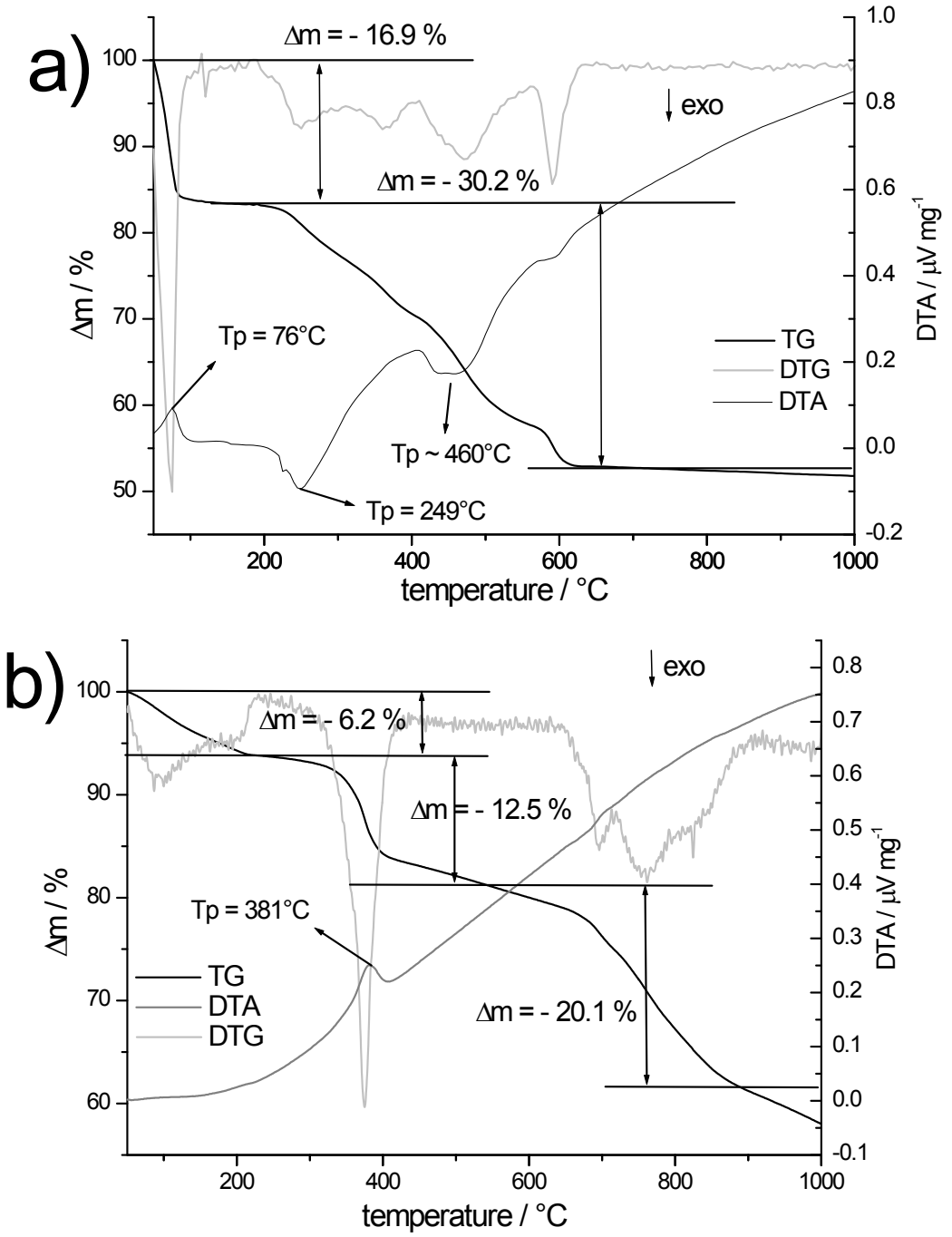


Figure S24a-b. DTA-TG curves of compound **I** without (a) and with (b) evacuating the sample chamber.

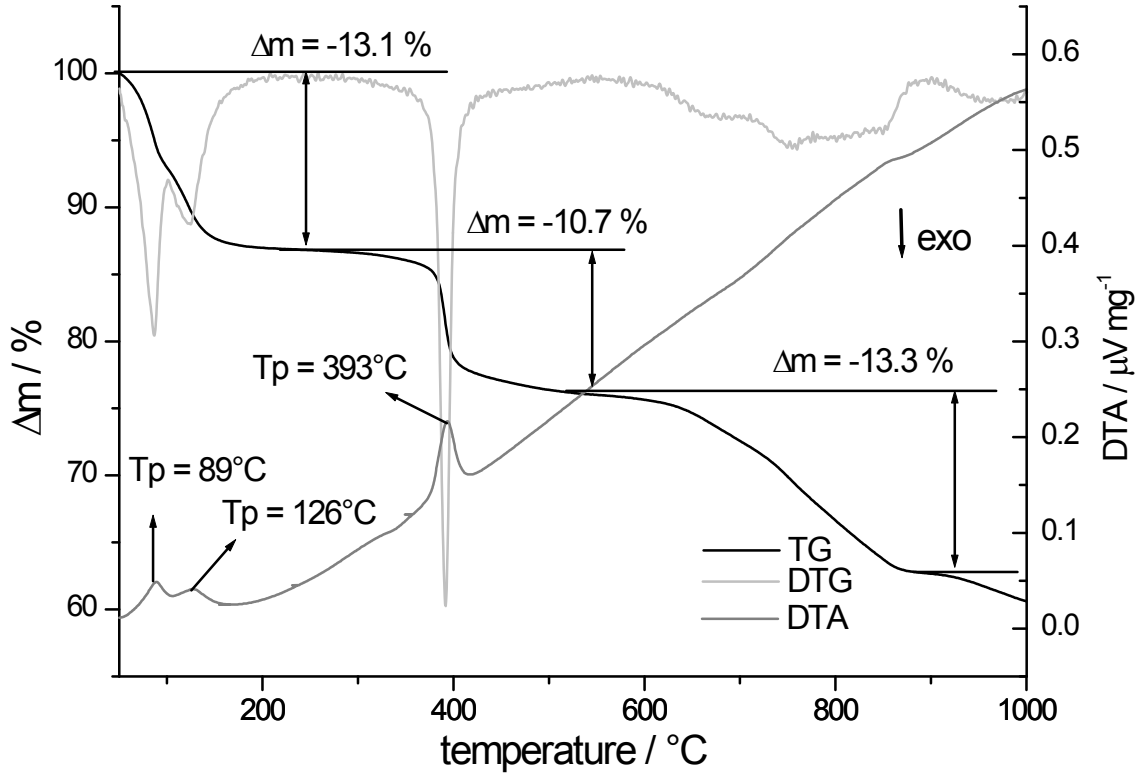


Figure S25. DTA-TG curves of compound **II**.

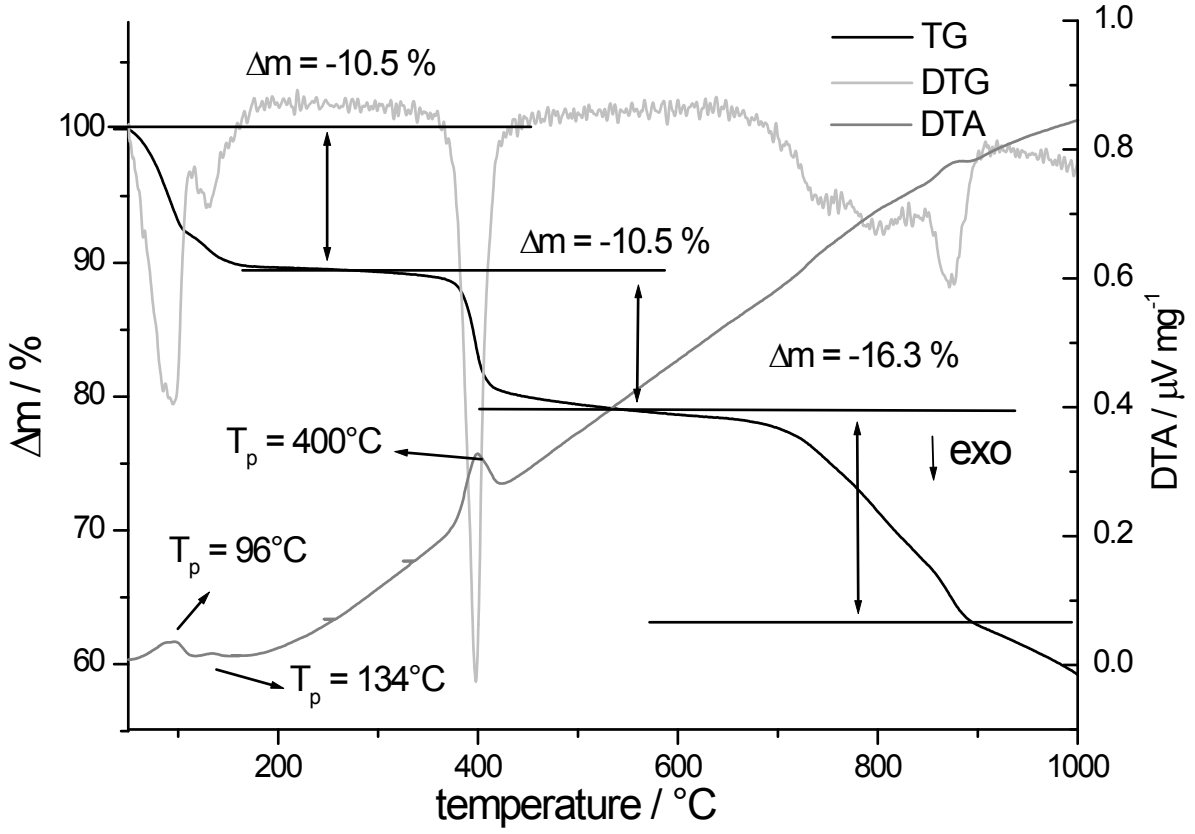


Figure S26. DTA-TG curves of compound **III**.

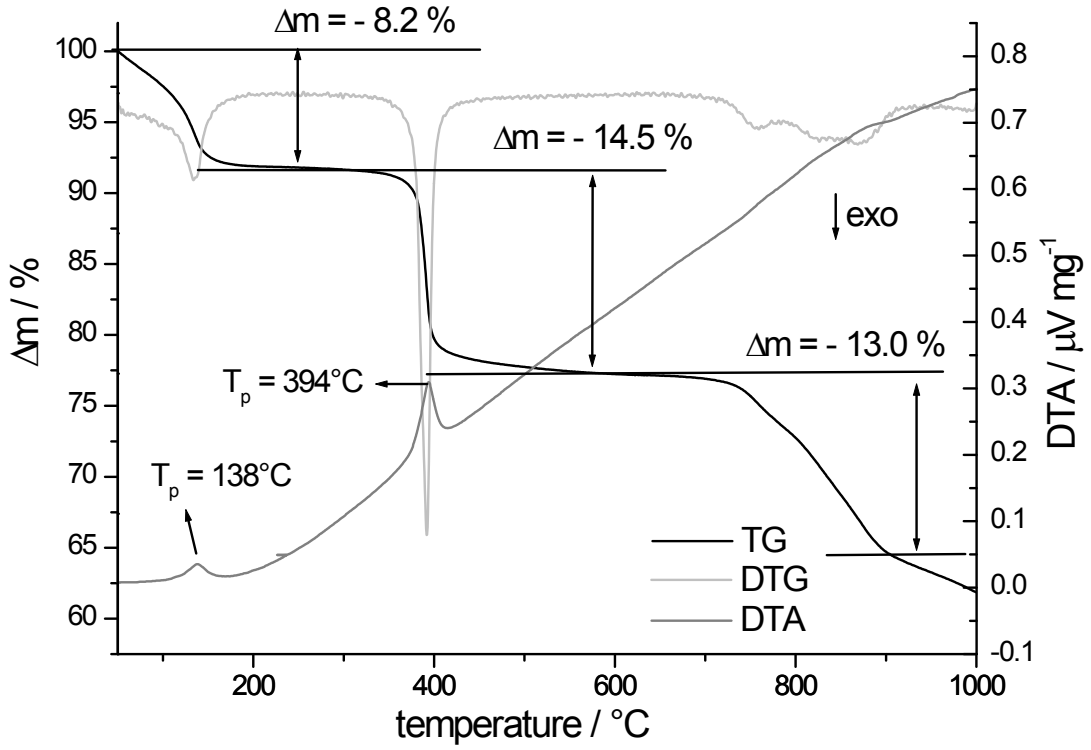


Figure S27. DTA-TG curves of compound **IV**.

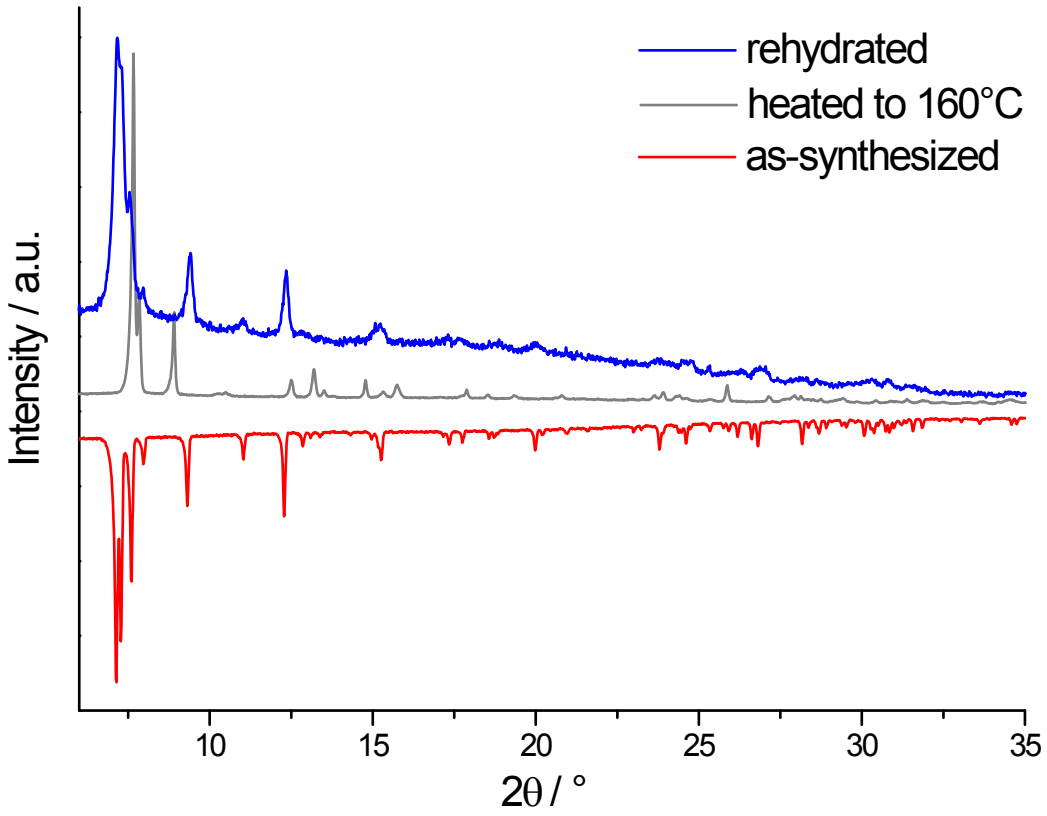


Figure S28. Comparison of XRDP of compound **I** as–synthesized (red), after heating to 160 °C (grey) and after rehydration experiment (blue).

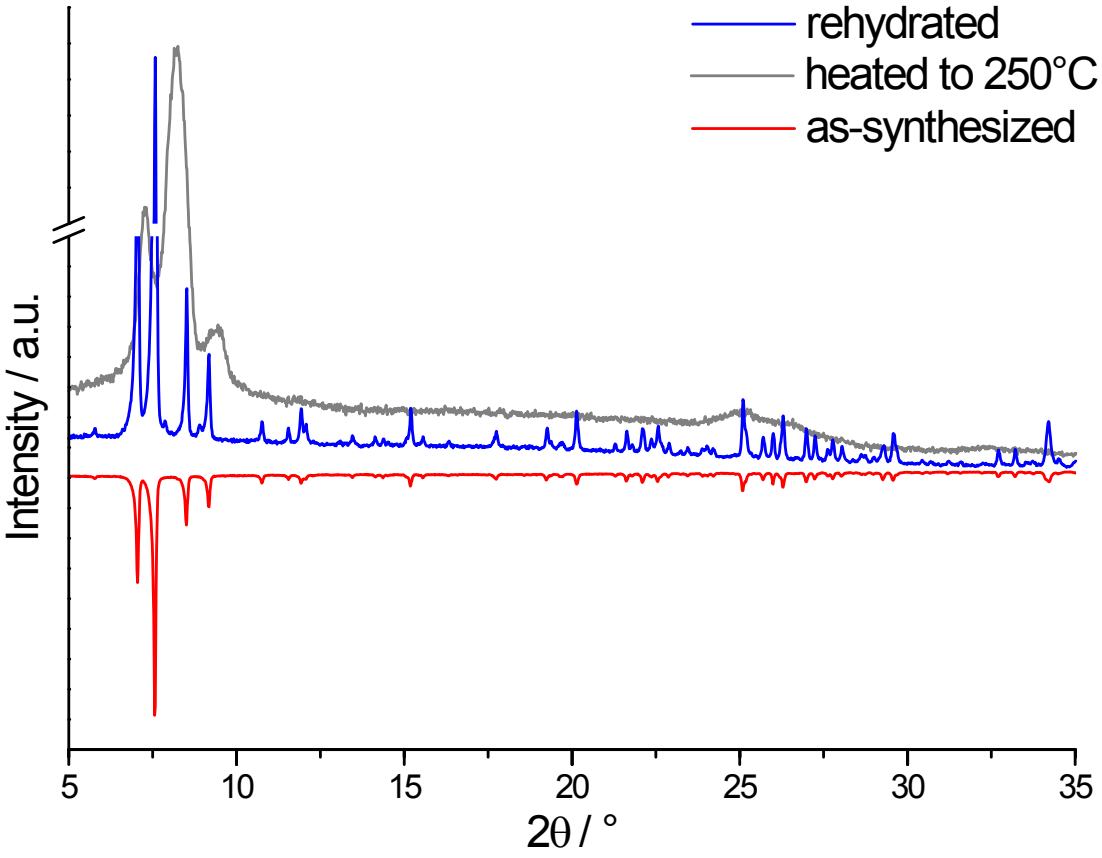


Figure S29. Comparison of XRDP of compound **II** as–synthesized (red), after heating to 250 °C (grey) and after rehydration experiment (blue).

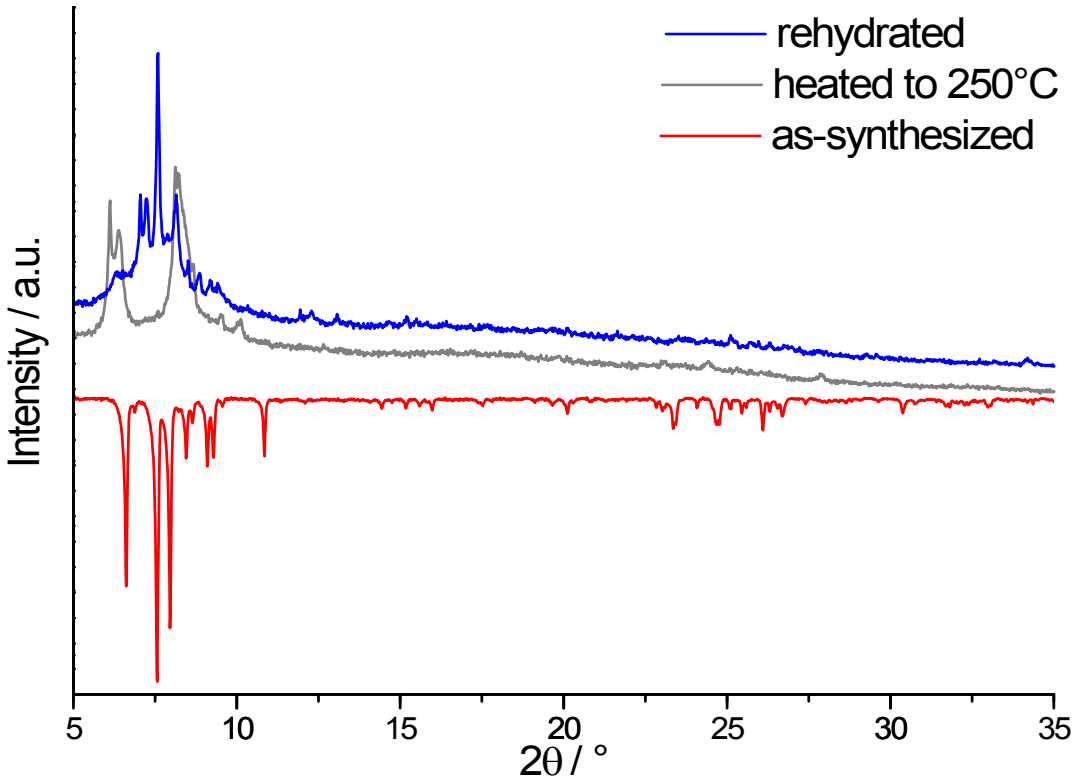


Figure S30. Comparison of XRDP of compound **III** as–synthesized (red), after heating to 250 °C (grey) and after rehydration experiment (blue).

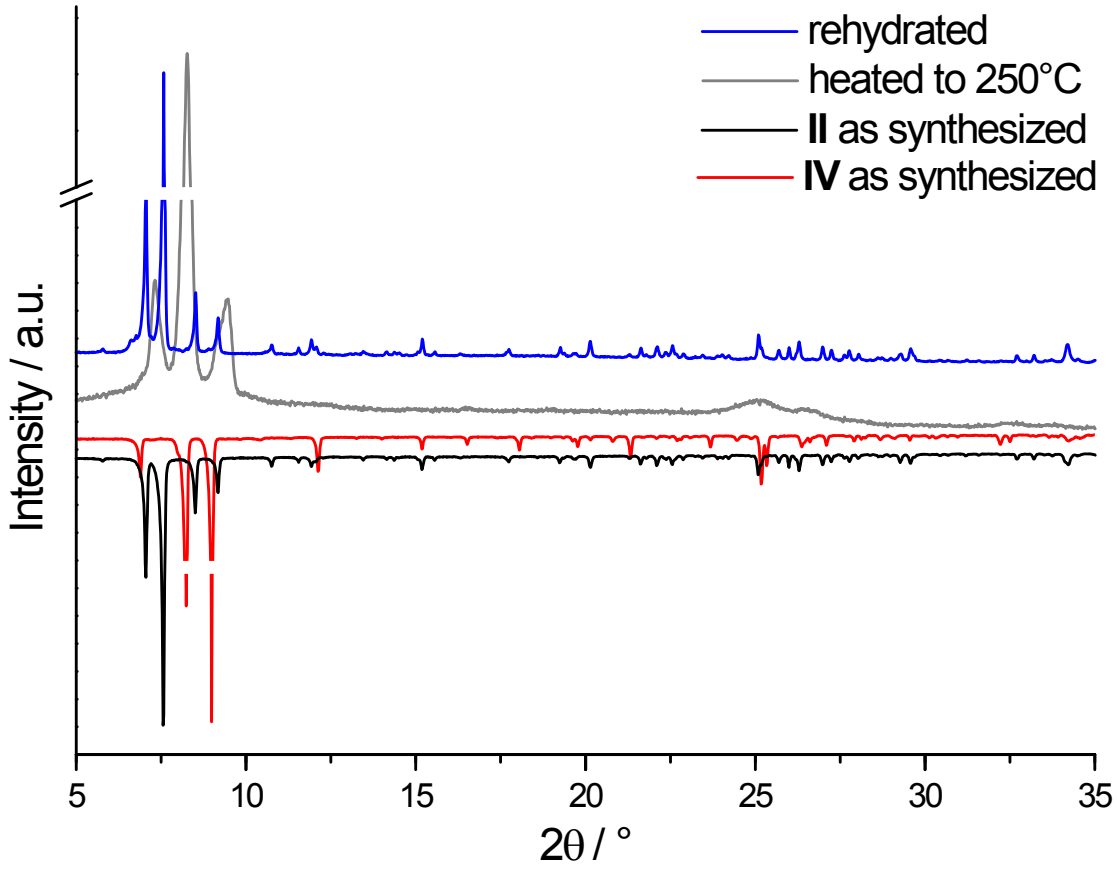


Figure S31. Comparison of XRDP of compound **II** (black) and **IV** (red) as–synthesized with the XRPD of **IV** after heating to 250 °C (grey) and after rehydration experiment (blue).

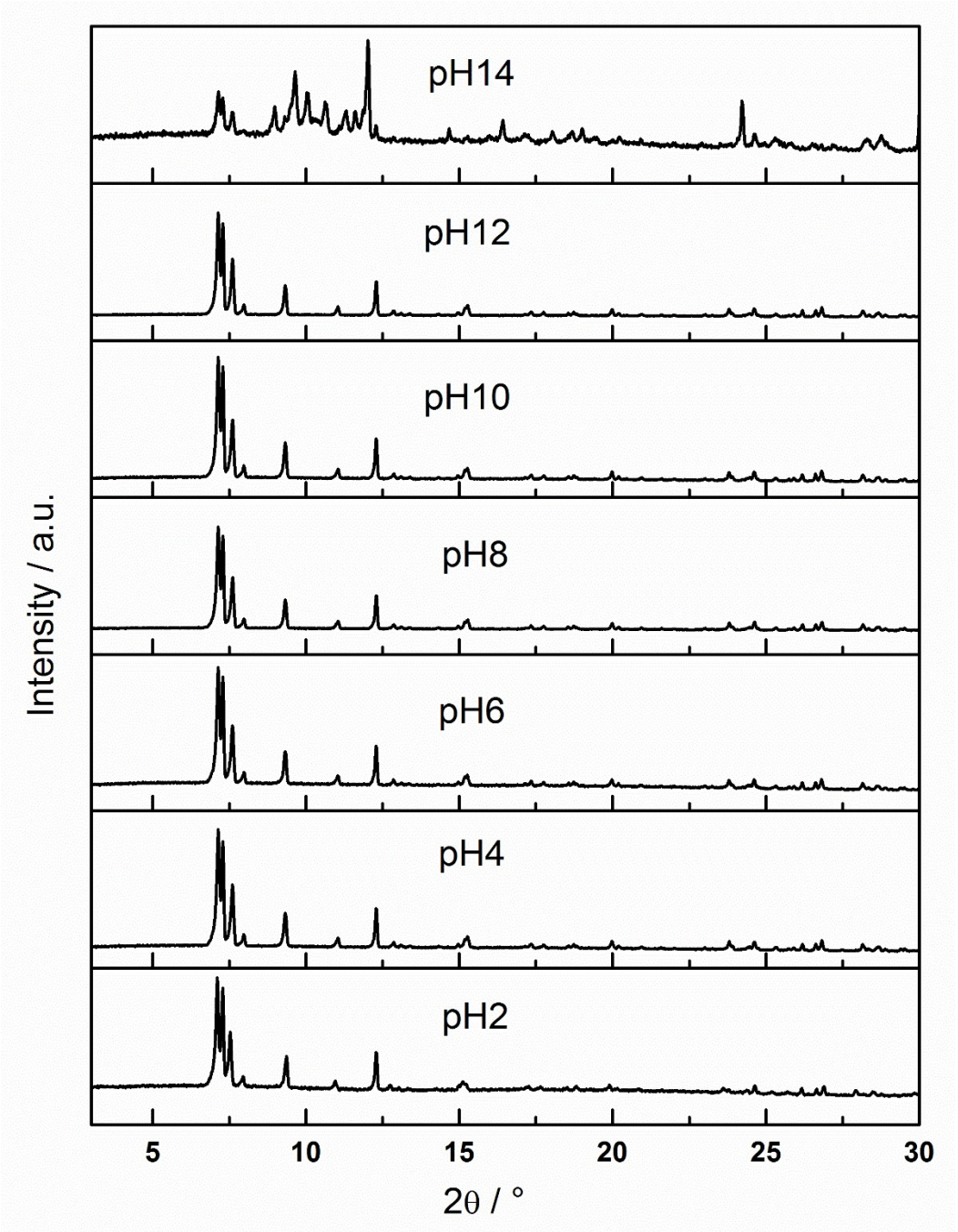


Figure S32. XRDP of compound **I** after immersing the samples in aqueous solutions of different pH values.

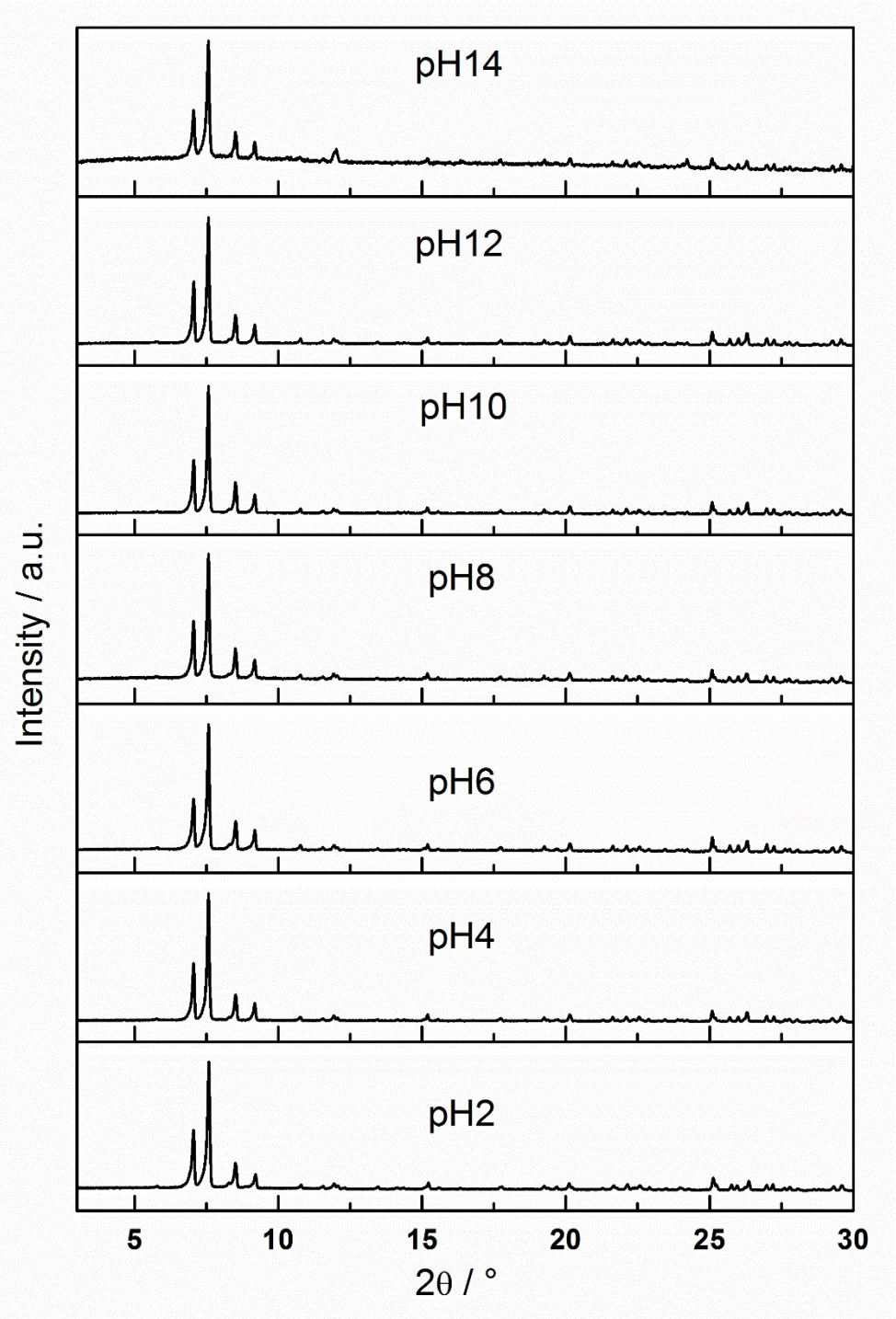


Figure S33. XRDP of compound **II** after immersing the samples in aqueous solutions of different pH values.

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