Supporting Information

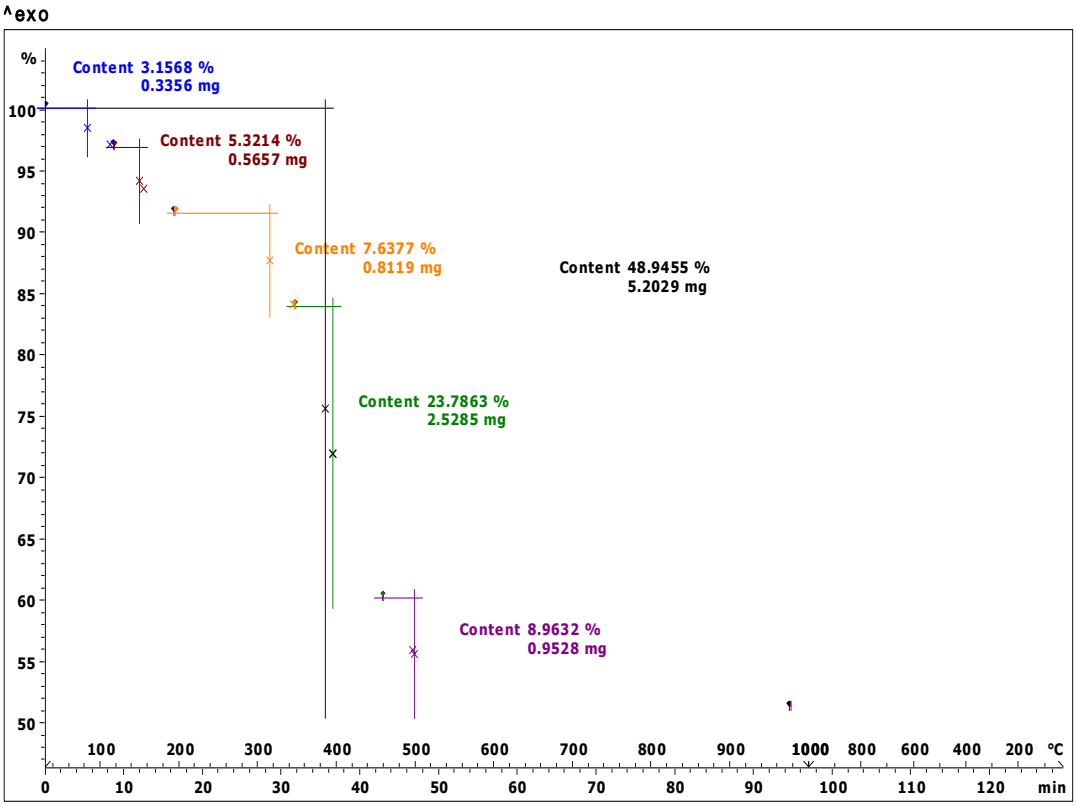

Figure S1: TGA of Mg–Al–NO_3 LDHs.

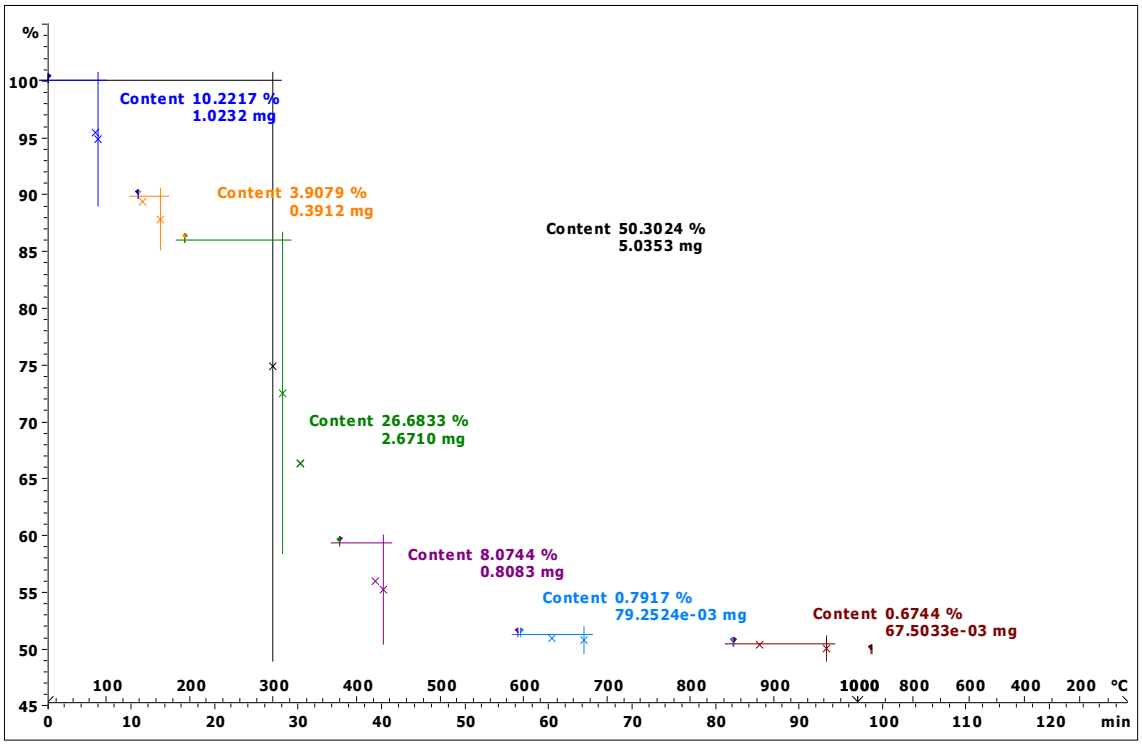

Figure S2: TGA of compound LDH-Complex **1**.

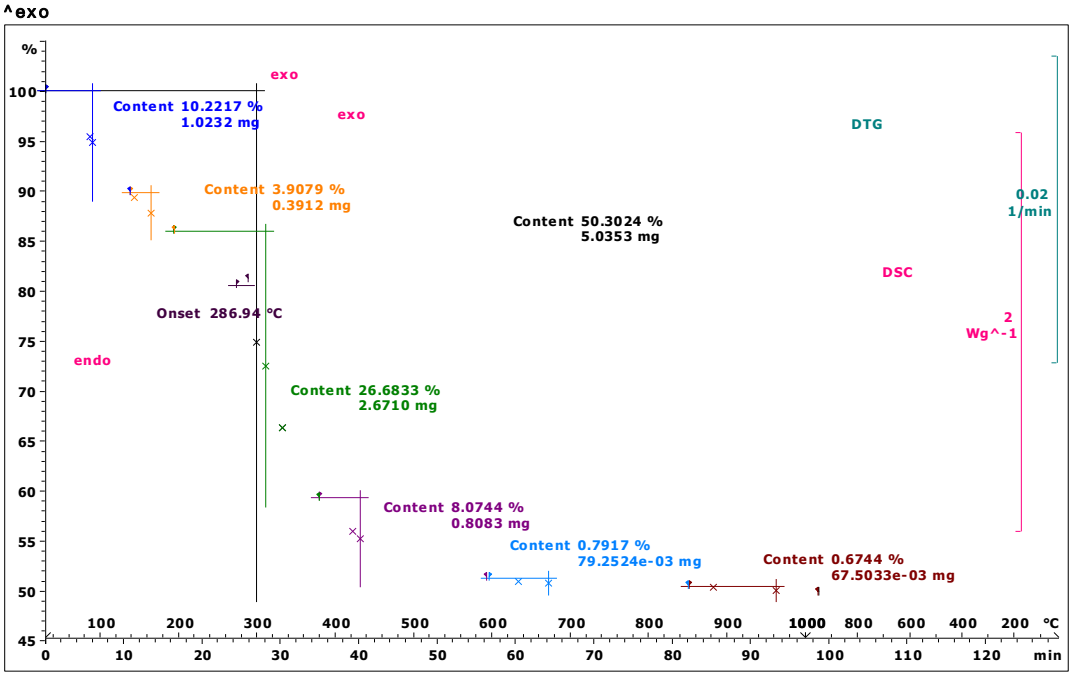

Figure S3: TGA (dark curve), DTG (green curve) and DSC (pink curve) of LDH-Complex **1**.

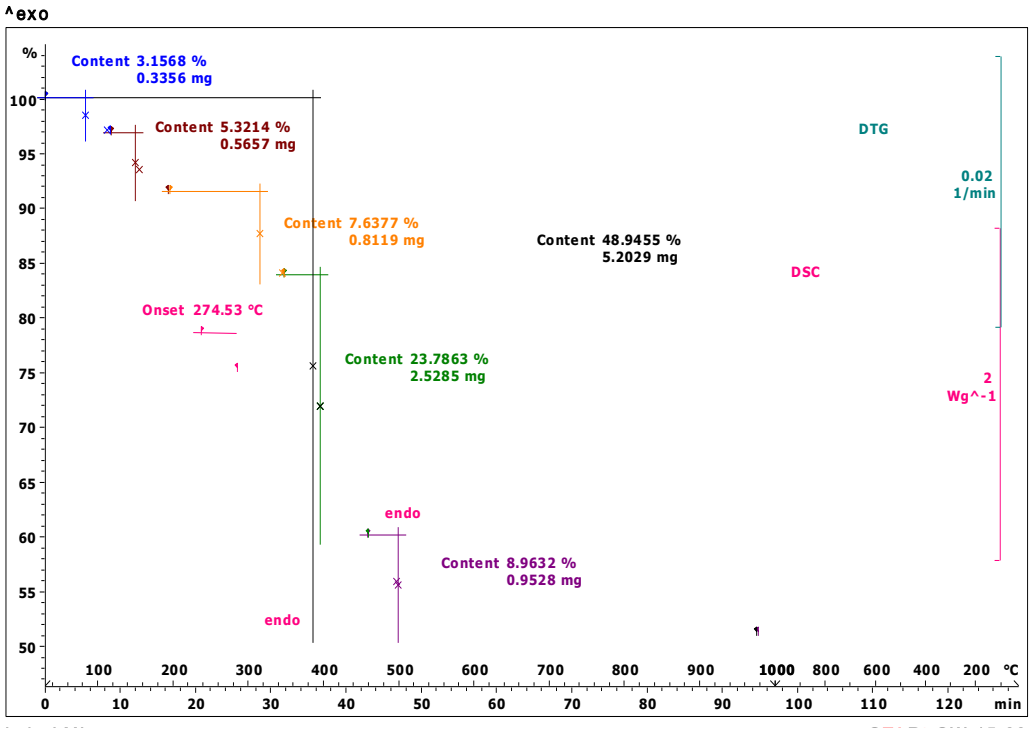

Figure S4: TGA (dark curve), DTG (green curve) and DSC (pink curve) of Mg–Al–NO_3 LDHs.

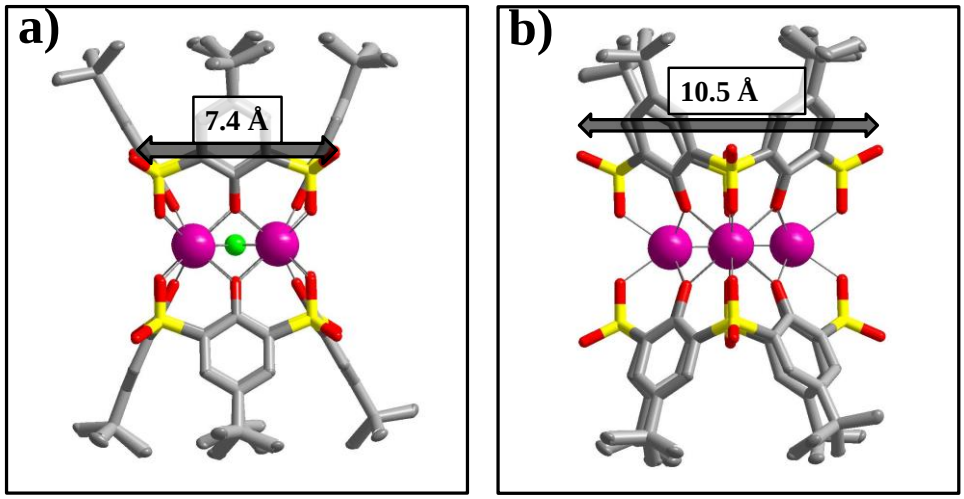

Figure S5: [(ThiaSO$_2$)$_2$(Mn^{II})$_4$F]K complex width dimension measured from single crystal X-Ray Diffraction structure in two directions.

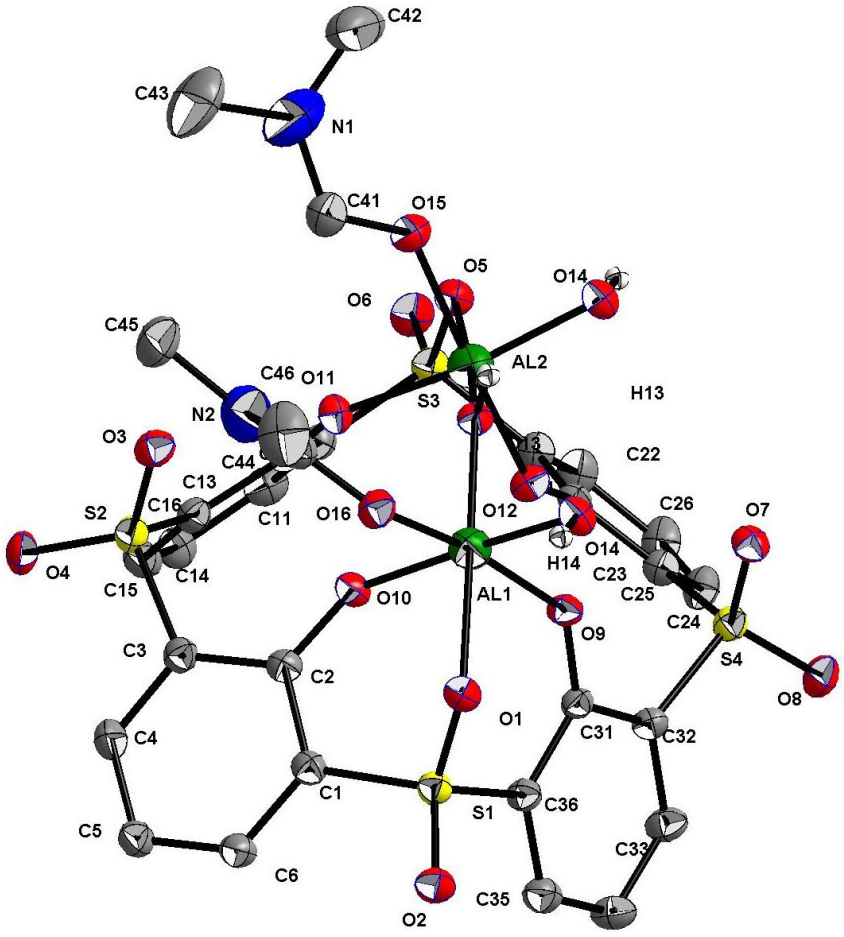

Figure S6: ORTEP[i] diagram of asymmetric unit of tetra-aluminium complex of Al$_4$(ThiaSO$_2$)$_2$ with thermal ellipsoids at 50% probability. Hydrogen atoms and tertbutyl groups are omitted for clarity.

Table S1: Crystal Data of $Al_4(ThiaSO_2)_2$ complex.

Formula	$C_{92}H_{120}Al_4N_4O_{32}S_8$	Z'	0.5
$D_{calc.}$/g cm^{-3}	1.157	Wavelength/Å	0.71073
μ/mm^{-1}	0.240	Radiation type	Mo K_α
Formula Weight	2158.31	θ_{min}/°	2.752
Color	colorless	θ_{max}/°	29.266
Shape	block	Measured Refl's.	68248
Size/mm^3	0.34 × 0.15 × 0.13	Ind't Refl's	15063
T/K	293.00	Refl's with I > 2(I)	8109
Crystal System	monoclinic	R_{int}	0.0862
Space Group	$P2_1/n$	Parameters	717
a/Å	13.9486(4)	Restraints	152
b/Å	22.9133(7)	Largest Peak	0.372
c/Å	20.0205(6)	Deepest Hole	-0.308
α/°	90	GooF	1.000
β/°	104.421(3)	wR_2 (all data)	0.1567
γ/°	90	wR_2	0.1327
V/Å^3	6197.1(3)	R_1 (all data)	0.1269
Z	2	R_1	0.0653

Table S2: Bond Lengths in Å for $Al_4(ThiaSO_2)_2$ complex.

Atom	Atom	Length/Å
S1	O1	1.4648(19)
S1	O2	1.429(2)
S1	C1	1.742(3)
S1	C36	1.755(3)
S2	O3	1.437(2)
S2	O4	1.439(2)
S2	C3	1.779(3)
S2	C16	1.769(3)
S3	O5	1.464(2)
S3	O6	1.429(2)
S3	C12	1.749(3)
S3	C21	1.743(3)
S4	O7	1.429(2)
S4	O8	1.442(2)
S4	C23	1.772(3)
S4	C32	1.766(3)
Al1	O1	2.068(2)
Al1	O9	1.837(2)
Al1	O10	1.8799(19)
Al1	O13	1.848(2)
Al1	O14[1]	1.871(2)
Al1	O16	1.928(2)
Al2	O5	2.107(2)
Al2	O11	1.8428(19)
Al2	O12	1.881(2)
Al2	O13	1.827(2)
Al2	O14	1.849(2)
Al2	O15	1.927(2)
O9	C31	1.285(3)
O10	C2	1.299(3)
O11	C11	1.287(3)
O12	C22	1.303(3)
O15	C41	1.223(4)
O16	C44	1.247(3)
N1	C41	1.318(4)
N1	C42	1.427(5)
N1	C43	1.447(5)
N2	C44	1.314(4)
N2	C45	1.458(4)
N2	C46	1.450(5)
C1	C2	1.421(4)
C1	C6	1.381(4)
C2	C3	1.411(4)
C3	C4	1.387(4)

Atom	Atom	Length/Å
C4	C5	1.384(4)
C5	C6	1.392(4)
C5	C7	1.538(4)
C7	C8	1.523(5)
C7	C9	1.537(5)
C7	C10	1.521(5)
C11	C12	1.420(4)
C11	C16	1.420(4)
C12	C13	1.391(4)
C13	C14	1.391(4)
C14	C15	1.379(4)
C14	C17	1.537(4)
C15	C16	1.383(4)
C17	C18A	1.539(6)
C17	C18B	1.502(7)
C17	C19A	1.536(6)
C17	C19B	1.536(6)
C17	C20A	1.507(6)
C17	C20B	1.530(7)
C21	C22	1.423(4)
C21	C26	1.378(4)
C22	C23	1.405(4)
C23	C24	1.395(4)
C24	C25	1.386(4)
C25	C26	1.385(4)
C25	C27	1.537(5)
C27	C28A	1.551(6)
C27	C28B	1.497(7)
C27	C29A	1.516(6)
C27	C29B	1.541(7)
C27	C30A	1.496(6)
C27	C30B	1.501(7)
C31	C32	1.432(4)
C31	C36	1.420(4)
C32	C33	1.389(4)
C33	C34	1.390(4)
C34	C35	1.385(4)
C34	C37	1.532(4)
C35	C36	1.392(4)
C37	C38	1.536(6)
C37	C39	1.518(6)
C37	C40	1.511(5)

Table S3: Bond Angles in ° for $Al_4(ThiaSO_2)_2$ complex.

Atom	Atom	Atom	Angle/°
O1	S1	C1	107.36(12)
O1	S1	C36	106.83(12)
O2	S1	O1	116.07(12)
O2	S1	C1	108.58(13)
O2	S1	C36	109.63(13)
C1	S1	C36	108.10(13)
O3	S2	O4	116.68(13)
O3	S2	C3	110.65(13)
O3	S2	C16	110.97(13)
O4	S2	C3	105.45(13)
O4	S2	C16	106.01(13)

Atom	Atom	Atom	Angle/°
C16	S2	C3	106.44(13)
O5	S3	C12	108.18(13)
O5	S3	C21	106.42(12)
O6	S3	O5	116.73(13)
O6	S3	C12	108.99(13)
O6	S3	C21	109.03(13)
C21	S3	C12	107.09(14)
O7	S4	O8	116.74(12)
O7	S4	C23	109.28(13)
O7	S4	C32	110.13(13)
O8	S4	C23	106.13(13)

Atom	Atom	Atom	Angle/°
O8	S4	C32	106.24(13)
C32	S4	C23	107.92(13)
O9	Al1	O1	86.21(8)
O9	Al1	O10	93.38(9)
O9	Al1	O13	94.11(9)
O9	Al1	O14[1]	91.57(9)
O9	Al1	O16	168.08(10)
O10	Al1	O1	87.84(8)
O10	Al1	O16	89.57(9)
O13	Al1	O1	179.26(9)
O13	Al1	O10	91.48(9)
O13	Al1	O14[1]	94.38(9)
O13	Al1	O16	97.36(9)
O14[1]	Al1	O1	86.27(9)
O14[1]	Al1	O10	172.05(10)
O14[1]	Al1	O16	84.36(9)
O16	Al1	O1	82.36(9)
O11	Al2	O5	84.44(8)
O11	Al2	O12	92.13(9)
O11	Al2	O14	169.81(10)
O11	Al2	O15	88.13(9)
O12	Al2	O5	86.98(8)
O12	Al2	O15	168.76(10)
O13	Al2	O5	175.16(9)
O13	Al2	O11	93.01(9)
O13	Al2	O12	97.25(9)
O13	Al2	O14	96.06(9)
O13	Al2	O15	93.97(9)
O14	Al2	O5	86.17(9)
O14	Al2	O12	91.32(9)
O14	Al2	O15	86.63(10)
O15	Al2	O5	81.85(9)
S1	O1	Al1	119.95(11)
S3	O5	Al2	118.97(11)
C31	O9	Al1	134.83(17)
C2	O10	Al1	136.06(18)
C11	O11	Al2	133.88(18)
C22	O12	Al2	135.34(18)
Al2	O13	Al1	138.42(11)
Al2	O14	Al1[1]	140.23(12)
C41	O15	Al2	129.9(2)
C44	O16	Al1	125.7(2)
C41	N1	C42	120.9(3)
C41	N1	C43	119.5(4)
C42	N1	C43	119.6(4)
C44	N2	C45	120.5(3)
C44	N2	C46	121.0(3)
C46	N2	C45	118.1(3)
C2	C1	S1	117.8(2)
C6	C1	S1	119.5(2)
C6	C1	C2	122.8(3)
O10	C2	C1	122.7(2)
O10	C2	C3	122.9(3)
C3	C2	C1	114.4(2)
C2	C3	S2	122.3(2)
C4	C3	S2	116.0(2)
C4	C3	C2	121.7(3)
C5	C4	C3	123.2(3)
C4	C5	C6	115.9(3)
C4	C5	C7	123.0(3)
C6	C5	C7	121.0(3)
C1	C6	C5	122.0(3)
C8	C7	C5	111.6(3)

Atom	Atom	Atom	Angle/°
C8	C7	C9	108.3(3)
C9	C7	C5	108.0(3)
C10	C7	C5	109.8(3)
C10	C7	C8	109.2(3)
C10	C7	C9	109.9(3)
O11	C11	C12	124.4(3)
O11	C11	C16	122.0(3)
C12	C11	C16	113.6(3)
C11	C12	S3	120.9(2)
C13	C12	S3	115.8(2)
C13	C12	C11	123.3(3)
C14	C13	C12	121.5(3)
C13	C14	C17	121.3(3)
C15	C14	C13	116.0(3)
C15	C14	C17	122.6(3)
C14	C15	C16	123.5(3)
C11	C16	S2	122.5(2)
C15	C16	S2	115.5(2)
C15	C16	C11	122.0(3)
C14	C17	C18A	111.4(4)
C18B	C17	C14	110.4(5)
C18B	C17	C19B	112.8(7)
C18B	C17	C20B	111.8(8)
C19A	C17	C14	109.2(4)
C19A	C17	C18A	105.1(6)
C19B	C17	C14	110.8(4)
C20A	C17	C14	111.0(5)
C20A	C17	C18A	105.8(7)
C20A	C17	C19A	114.2(7)
C20B	C17	C14	106.1(5)
C20B	C17	C19B	104.7(7)
C22	C21	S3	117.1(2)
C26	C21	S3	119.7(2)
C26	C21	C22	123.2(3)
O12	C22	C21	121.5(3)
O12	C22	C23	124.3(3)
C23	C22	C21	114.2(3)
C22	C23	S4	121.4(2)
C24	C23	S4	116.8(2)
C24	C23	C22	121.6(3)
C25	C24	C23	123.0(3)
C24	C25	C27	122.8(3)
C26	C25	C24	116.2(3)
C26	C25	C27	121.0(3)
C21	C26	C25	121.7(3)
C25	C27	C28A	108.2(4)
C25	C27	C29B	105.0(5)
C28B	C27	C25	116.1(6)
C28B	C27	C29B	109.6(10)
C28B	C27	C30B	114.6(10)
C29A	C27	C25	106.9(4)
C29A	C27	C28A	107.8(6)
C30A	C27	C25	114.3(4)
C30A	C27	C28A	103.9(6)
C30A	C27	C29A	115.4(6)
C30B	C27	C25	109.3(6)
C30B	C27	C29B	100.7(10)
O9	C31	C32	121.6(2)
O9	C31	C36	125.1(2)
C36	C31	C32	113.3(2)
C31	C32	S4	122.2(2)
C33	C32	S4	115.6(2)
C33	C32	C31	122.2(3)

Atom	Atom	Atom	Angle/°
C32	C33	C34	122.9(3)
C33	C34	C37	121.0(3)
C35	C34	C33	116.2(3)
C35	C34	C37	122.5(3)
C34	C35	C36	121.9(3)
C31	C36	S1	120.5(2)
C35	C36	S1	115.9(2)
C35	C36	C31	123.4(3)
C34	C37	C38	110.2(3)
C39	C37	C34	107.8(3)
C39	C37	C38	109.1(4)
C40	C37	C34	112.5(3)
C40	C37	C38	107.7(4)
C40	C37	C39	109.6(4)
O15	C41	N1	122.9(3)
O16	C44	N2	122.6(3)

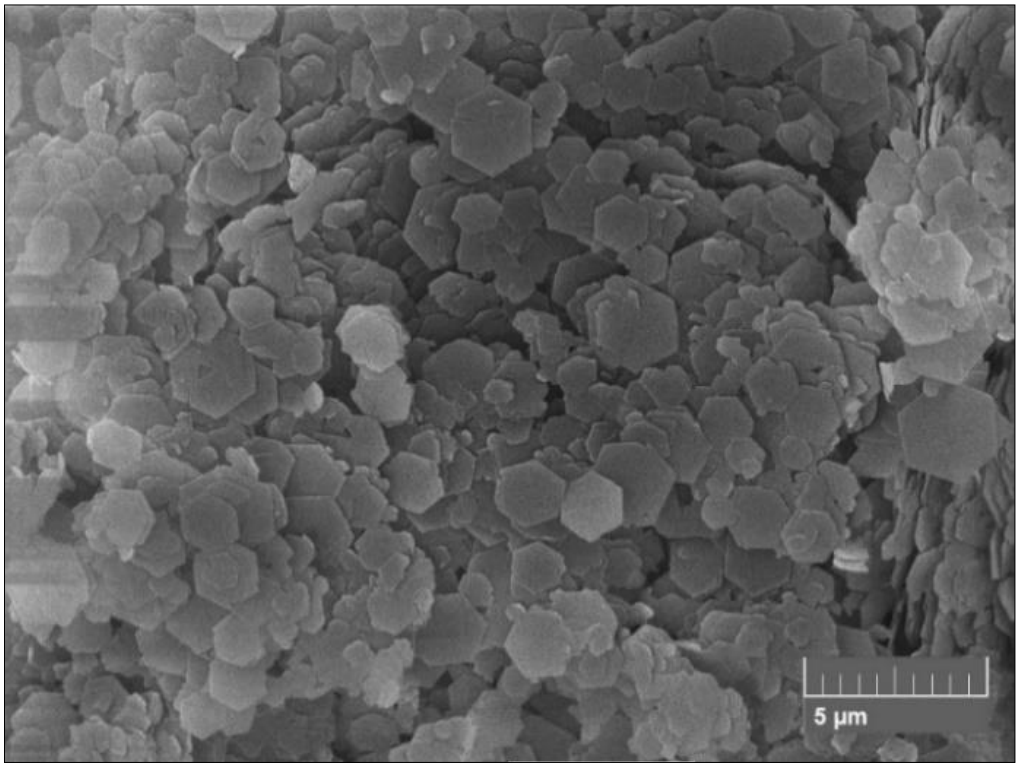

Figure S7: SEM images of LDH-NO_3**.**

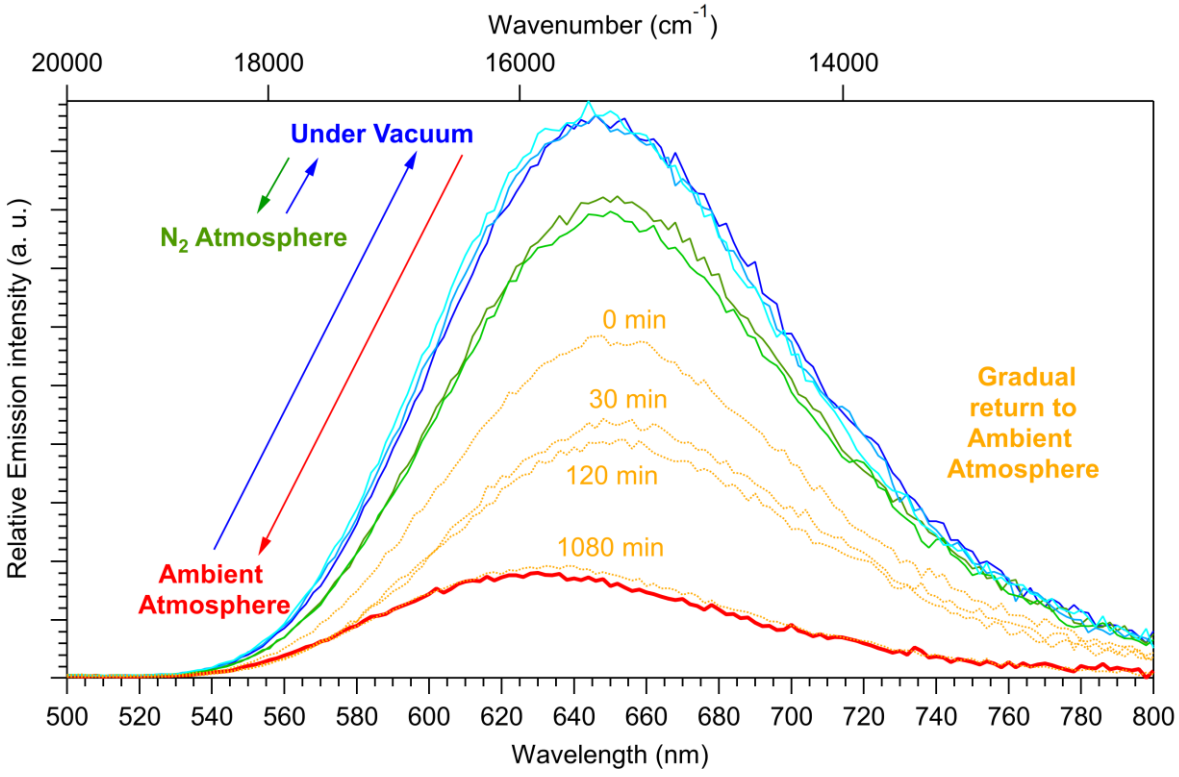

Figure S8: Solid state normalized emission (λex = 360 nm, T=293K) spectra with O_2, vacuum or N_2 atmosphere after storage of compound **1** for one year in the ambient atmosphere.

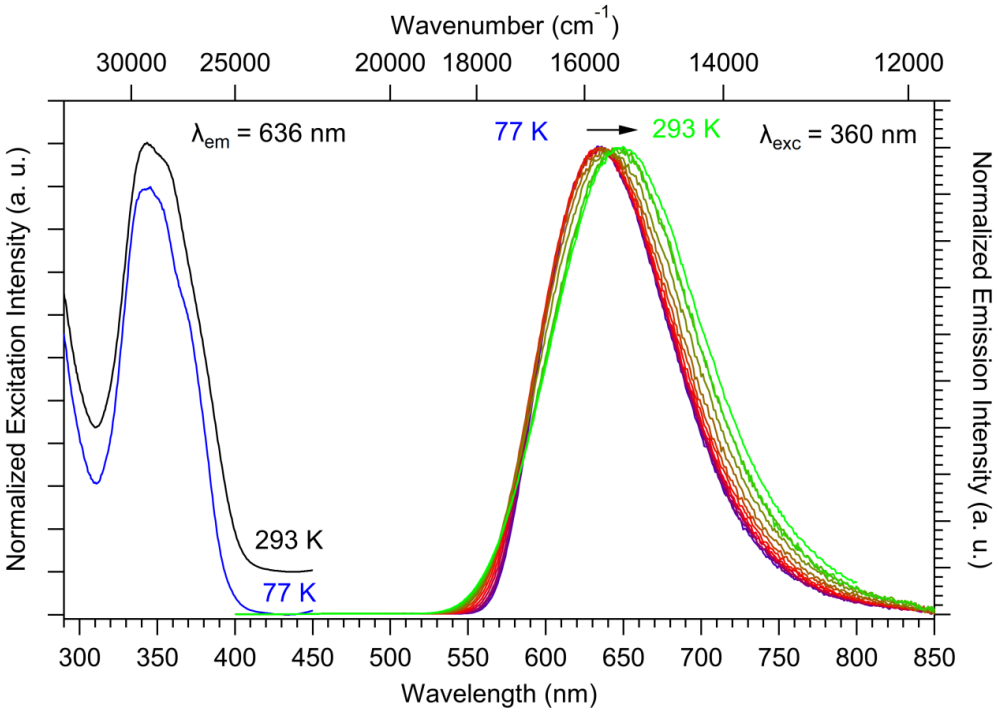

Figure S9: Solid-state normalized excitation (λ_{em} = 636 nm) and emission spectra (λ_{em} = 360 nm) *vs* temperature (77 - 293 K) of **1** with N_2 atmosphere. The excitation spectrum at 293 K is shifted by +0.01 on the normalized y-axis for clarity.

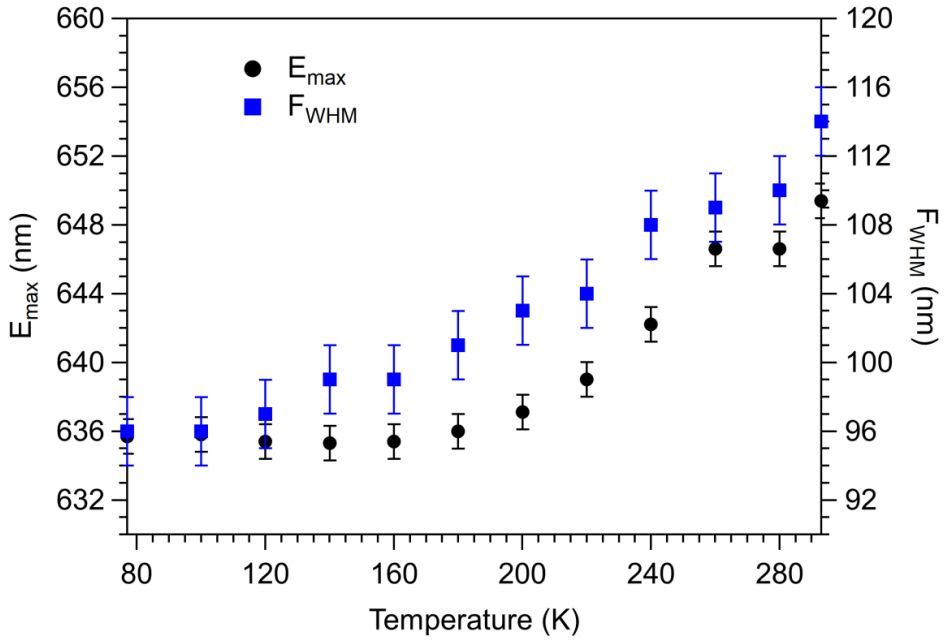

Figure S10: The energy band maxima E_{max} (left axis, in nm) and F_{WHM} (right axis, in nm) *vs* temperature (77 - 293 K) upon photoexcitation at 360 nm of **1** with N_2 atmosphere. Error bar = 1 or 2 nm for E_{max} and F_{WHM}, respectively.

[i] L. J. Farrugia, *J. Appl. Crystallogr.*, **45** (2012) 849.