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SUPPLEMENTARY MATERIAL

A Series of Early Lanthanide Chloranilate Frameworks with a Square Grid Topology

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Table S1. Crystal data and structure refinement details for **1, 2** and **3**.

	$(Et_4N)[La(can)_2(H_2O)]$ (**1**)	$(Et_4N)[Ce(can)_2(H_2O)]$ (**2**)	$(Et_4N)[Nd(can)_2(H_2O)]$ (**3**)
Formula	$C_{20}H_{21}Cl_4LaNO_9$	$C_{20}H_{21}CeCl_4NO_9$	$C_{40}H_{42}Cl_8N_2Nd_2O_{18}$
M/g mol^{-1}	700.09	701.30	1410.83
Temperature (K)	100(2)	100(2)	100(2)
Crystal system	Tetragonal	Tetragonal	Tetragonal
Space Group	*I*4/*m* (#87)	*I*4/*m* (#87)	*I*4/*m* (#87)
Crystal size (mm^3)	0.08 × 0.08 × 0.03	0.08 × 0.08 × 0.02	0.06 × 0.05 × 0.02
Crystal Colour	Purple	Purple	Purple
Crystal Habit	Plate	Plate	Plate
a (Å)	12.7822(5)	12.71120(10)	12.622(3)
b (Å)	12.7822(5)	12.71120(10)	12.622(3)
c (Å)	19.8412(8)	19.9142(4)	19.977(4)
V (Å^3)	3241.7(3)	3217.63(8)	3182.7(14)
Z	4	4	2
ρ_{calc} (mg/mm^3)	1.434	1.448	1.476
λ(CuKα)	1.54178 Å	1.54178 Å	0.71073 Å (MoKα)
μ(CuKα)	13.571 mm^{-1}	14.348 mm^{-1}	2.007 mm^{-1}
T(SADABS)$_{min,max}$	0.6059, 0.7529	0.49613, 1.00000 (CrystAlisPro)	0.674, 0.746
Reflections collected	10032/1462 [R_{merge} = 0.0274]	5602/1673 [R_{merge} = 0.0926]	30310/2419 [R_{merge} = 0.113]
Data/parameters	1462/101	1673/97	2419/95
Final R indexes [all data]	R_1 = 0.0456, wR_2 = 0.1269	R_1 = 0.0608, wR_2 = 0.1585	R_1 = 0.0522, wR_2 = 0.1367
Goodness-of-fit on F^2	1.172	1.175	1.134
Residual Extrema	-1.27, 3.18 e$^-$Å^{-3}	-1.31, 3.26 e$^-$Å^{-3}	-1.61, 4.10 e$^-$Å^{-3}

Table S2. Crystal data and structure refinement details for **3a**, **4** and **5**.

Parameter	$(Et_4N)[Nd(can)_2]$ (**3a**)	$(Et_4N)[Sm(can)_2]$ (**4**)	$(Et_4N)[Eu(can)_2]$ (**5**)
Formula	$0.5(C_{24}Cl_8Nd_2O_{16})\cdot C_8H_{20}N$	$0.5(C_{24}Cl_8O_{16}Sm_2)\cdot C_8H_{20}N$	$0.5(C_{24}Cl_8Eu_2O_{16})\cdot C_8H_{20}N$
M/g mol^{-1}	688.41	694.52	696.13
Temperature (K)	100(2)	100(2)	100(2)
Crystal system	Tetragonal	Tetragonal	Tetragonal
Space Group	I_4/mcm (#140)	I_4/mcm (#140)	$I4/mcm$ (#140)
Crystal size (mm^3)	0.05 × 0.05 × 0.02	0.08 × 0.06 × 0.04	0.05 × 0.04 × 0.03
Crystal Colour	Purple	Purple	Purple
Crystal Habit	Plate	Plate	Plate
a (Å)	12.4513 (16)	12.383(2)	12.3159(19)
b (Å)	12.4513 (16)	12.383(2)	12.3159(19)
c (Å)	20.073 (3)	20.146(5)	20.117(4)
V ($Å^3$)	3112.0 (9)	3089.2(14)	3051.4 (11)
Z	4	4	4
ρ_{calc} (mg/mm^3)	1.469	1.493	1.515
λ(MoKα)	0.71073 Å	0.71073 Å	0.71073 Å
μ(MoKα)	2.05 mm^{-1}	2.28 mm^{-1}	2.44 mm^{-1}
T(SADABS)$_{min,max}$	0.701, 0.745	0.690, 0.747	0.680, 0.746
Reflections collected	1501/373 [R_{merge} = 0.0580]	28621/1709 [R_{merge} = 0.0480]	23529/1222 [R_{merge} = 0.0610]
Data/parameters	373/37	1709/51	1222/51
Final R indexes [all data]	R_1 = 0.0320, wR_2 = 0.081	R_1 = 0.0230, wR_2 = 0.061	R_1 = 0.0250, wR_2 = 0.069
Goodness-of-fit on F^2	1.09	1.16	1.20
Residual Extrema	-0.92, 0.54 $e^-Å^{-3}$	-0.55, 0.73 $e^-Å^{-3}$	-0.69, 0.60 $e^-Å^{-3}$

Table S3. Analysis of the possible coordination geometries using the SHAPE program for the 9-coordinate La^{III}, Ce^{III} and Nd^{III} structures, compounds **1**, **2** and **3**.

Geometry	Symmetry	1	2	3
EP-9	D_{9h}	37.821	38.124	38.195
OPY-9	C_{8v}	20.665	20.971	21.350
HBPY-9	D_{7h}	17.775	17.752	17.774
JTC-9	C_{3v}	17.616	17.497	17.378
JCCU-9	C_{4v}	6.799	6.730	6.799
CCU-9	C_{4v}	4.985	4.974	5.082
JCSAPR-9	C_{4v}	2.588	2.478	2.346
CSAPR-9	C_{4v}	**1.373**	**1.298**	**1.171**
JTCTPR-9	D_{3h}	4.435	4.325	4.199
TCTPR-9	D_{3h}	2.374	2.321	2.227
JTDIC-9	C_{3v}	12.139	12.190	12.288
HH-9	C_{2v}	11.237	11.220	11.324
MFF-9	C_s	2.285	2.202	2.067

EP-9 = Enneagon; OPY-9 = Octagonal pyramid; HBPY-9 = Heptagonal bipyramid; JTC-9 = Triangular cupola (J3) = trivacant cuboctahedron; JCCU-9 = Capped cube (Elongated square pyramid, J8); CCU-9 = Capped cube; JCSAPR-9 = Capped square antiprism (Gyroelongated square pyramid J10); CSAPR-9 = Capped square antiprism; JTCTPR-9 = Tricapped trigonal prism (J51); TCTPR-9 = Tricapped trigonal prism; JTDIC-9 = Tridiminished icosahedron (J63); HH-9 = Hula-hoop; MFF-9 = Muffin. The minima values are indicated in bold.

Table S4. Analysis of the possible coordination geometries using the SHAPE program for the 8-coordinate structures, compounds **3a**, **4** and **5**.

Geometry	Symmetry	3a	4	5
OP-8	D_{8h}	25.764	26.062	26.229
HPY-8	C_{7v}	25.926	25.815	25.731
HBPY-8	D_{6h}	13.407	13.388	13.413
CU-8	O_h	5.485	5.463	5.489
SAPR-8	D_{4d}	**1.467**	**1.412**	**1.358**
TDD-8	D_{2d}	2.578	2.518	2.475
JGBF-8	D_{2d}	15.385	15.395	15.410
JETBPY-8	D_{3h}	28.878	28.876	28.904
JBTPR-8	C_{2v}	4.269	4.216	4.162
BTPR-8	C_{2v}	3.692	3.638	3.584
JSD-8	D_{2d}	6.151	6.108	6.066
TT-8	T_d	6.386	6.364	6.391
ETBPY-8	D_{3h}	23.049	23.120	23.164

OP-8 = Octagon; HPY-8 = Heptagonal pyramid; HBPY-8 = Hexagonal bipyramid; CU-8 = Cube; SAPR-8 = Square antiprism; TDD-8 = Triangular dodecahedron; JGBF-8 = Johnson gyrobifastigium J26; JETBPY-8 = Johnson elongated triangular bipyramid J14; JBTPR-8 = Biaugmented trigonal prism J50; BTPR-8 = Biaugmented trigonal prism; JSD-8 = Snub diphenoid J84; TT-8 = Triakis tetrahedron; ETBPY-8 = Elongated trigonal bipyramid. The minima values are indicated in bold.

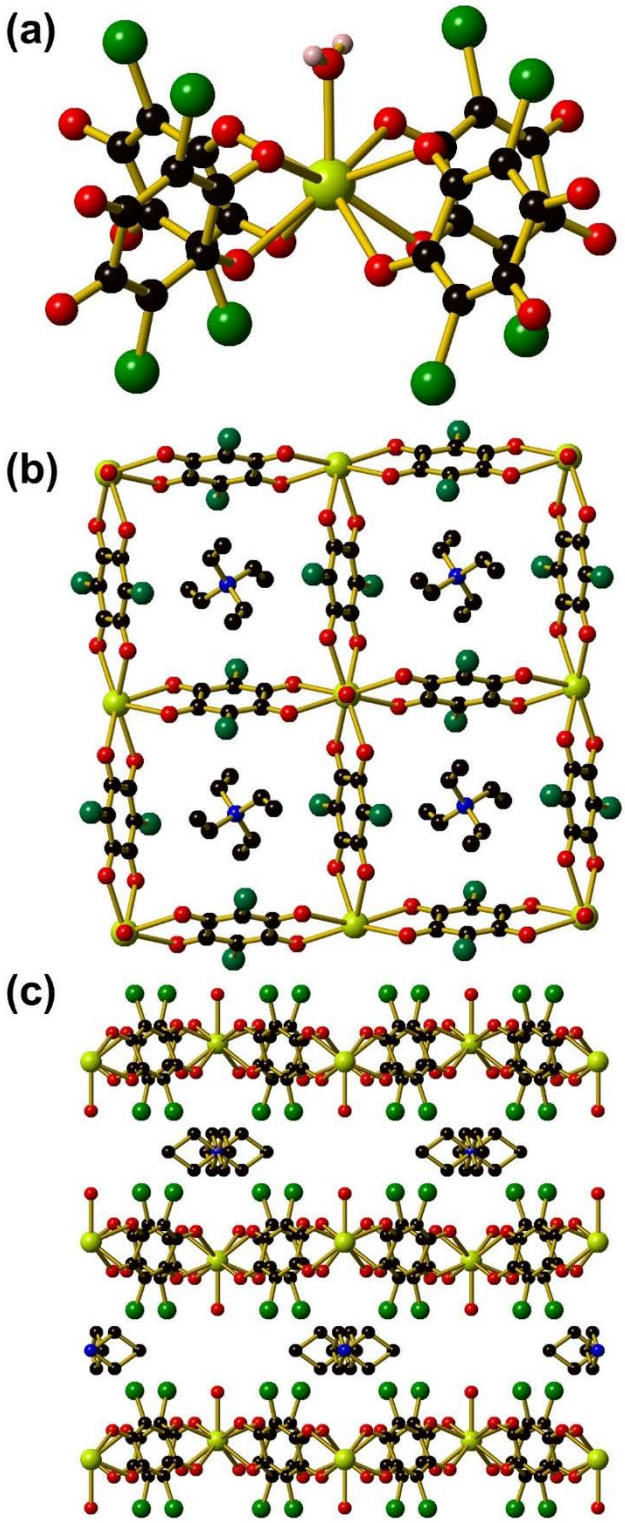

Figure S1. Crystal structure of $(Et_4N)[Ce(can)_2(H_2O)]$ (**2**), depicting (a) the coordination environment around the Ce^{III} centre, (b) the square grid lattice and (c) view along the *a* axis showing the alternating Et_4N^+ counterions. Yellow, red, blue, green, light pink and black spheres represent Ce, O, N, Cl, H and C atoms, respectively; H atoms are omitted for clarity in parts (b) and (c).

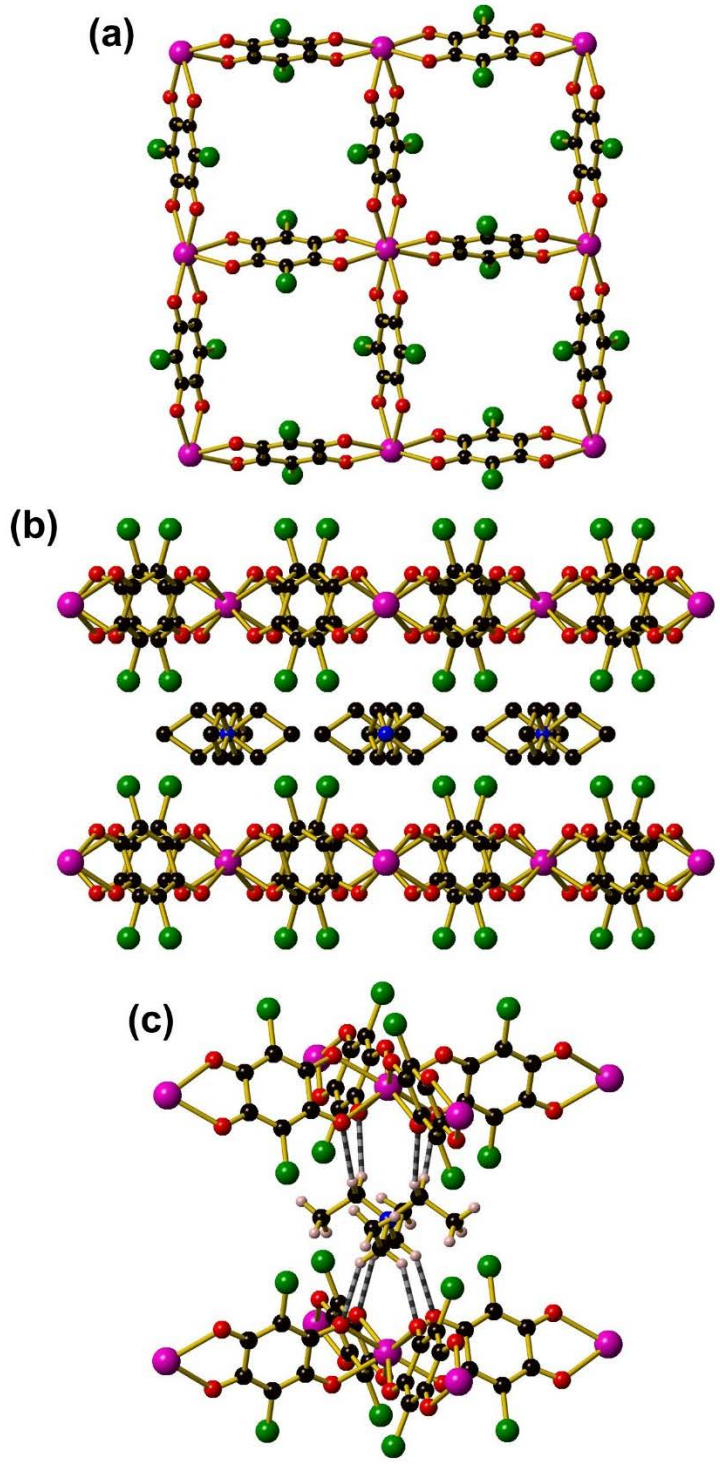

Figure S2. Crystal structure of $(Et_4N)[Eu(can)_2]$ (**5**) depicting (a) the square grid lattice, (b) view along the *a* axis showing the Et_4N^+ counterions and (d) the intermolecular interactions present between the Et_4N^+ cation and the framework. Pink, red, blue, green and black spheres represent Eu, O, N, Cl and C atoms, respectively. H atoms are omitted for clarity.

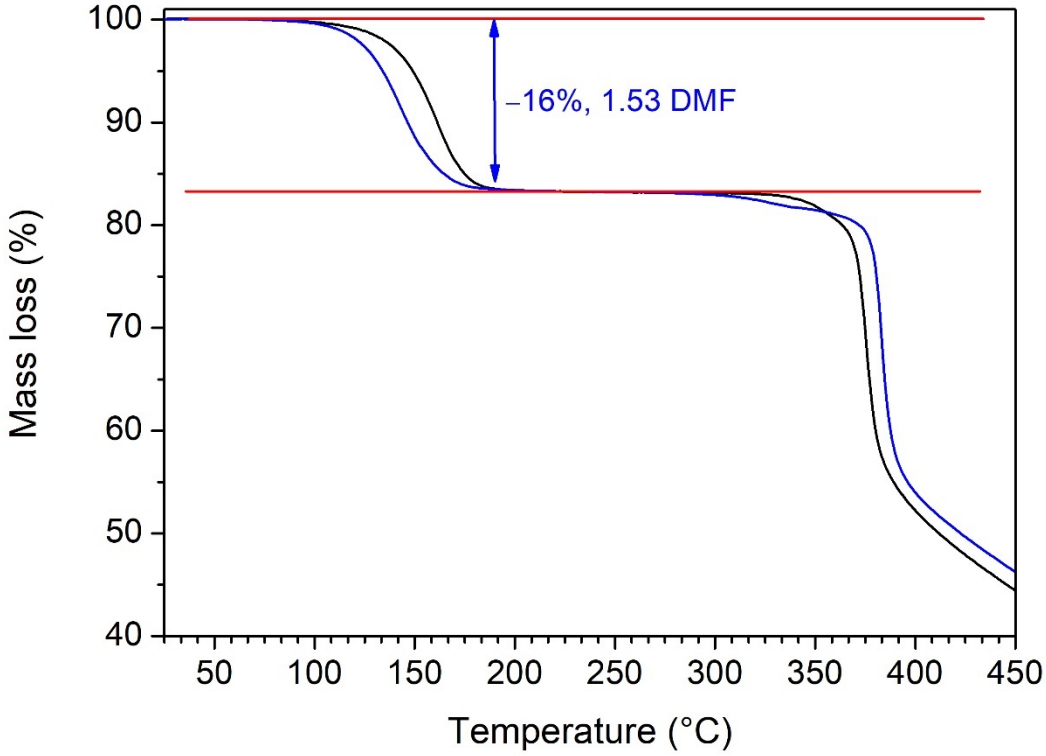

Figure S3. Thermal Gravimetric Analysis (TGA) of compounds **1** (black) and **2** (blue) from 25 to 450 °C.

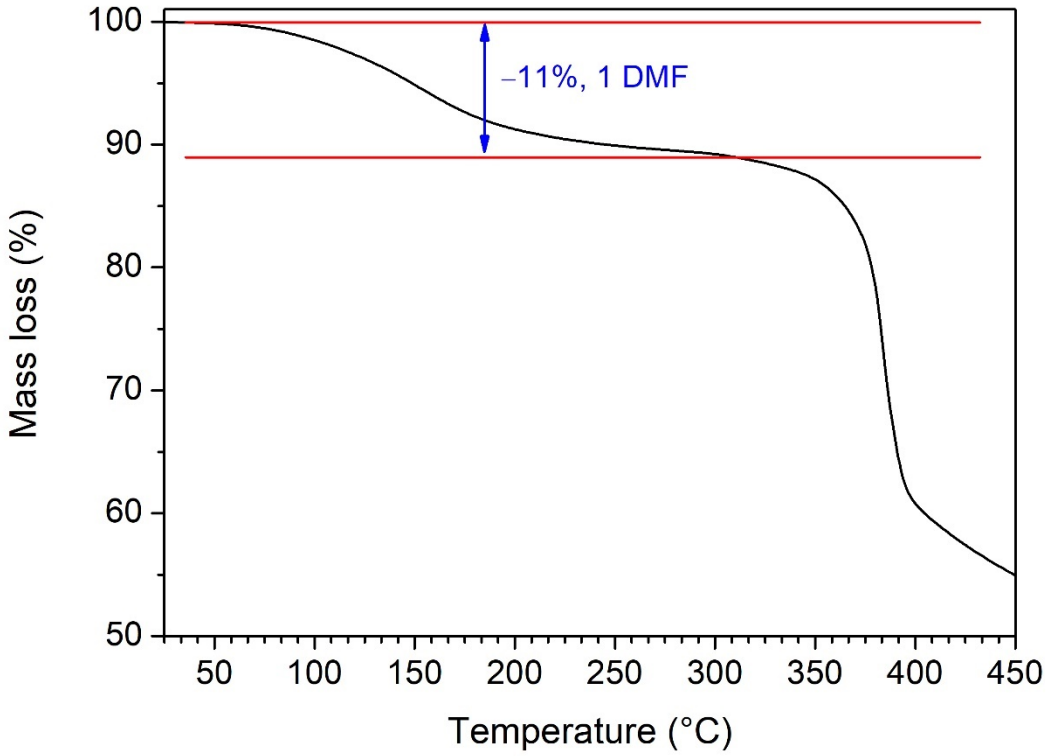

Figure S4. Thermal Gravimetric Analysis (TGA) of compound **4** from 25 to 450 °C.

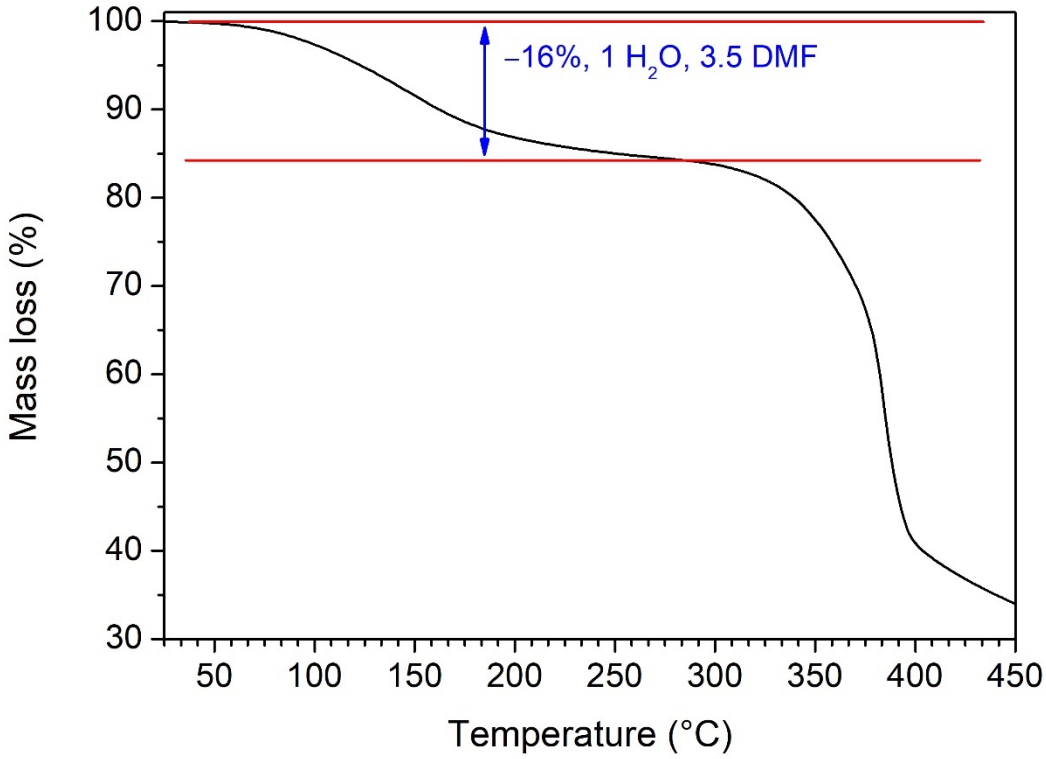

Figure S5. Thermal Gravimetric Analysis (TGA) of compound **5** from 25 to 450 °C.

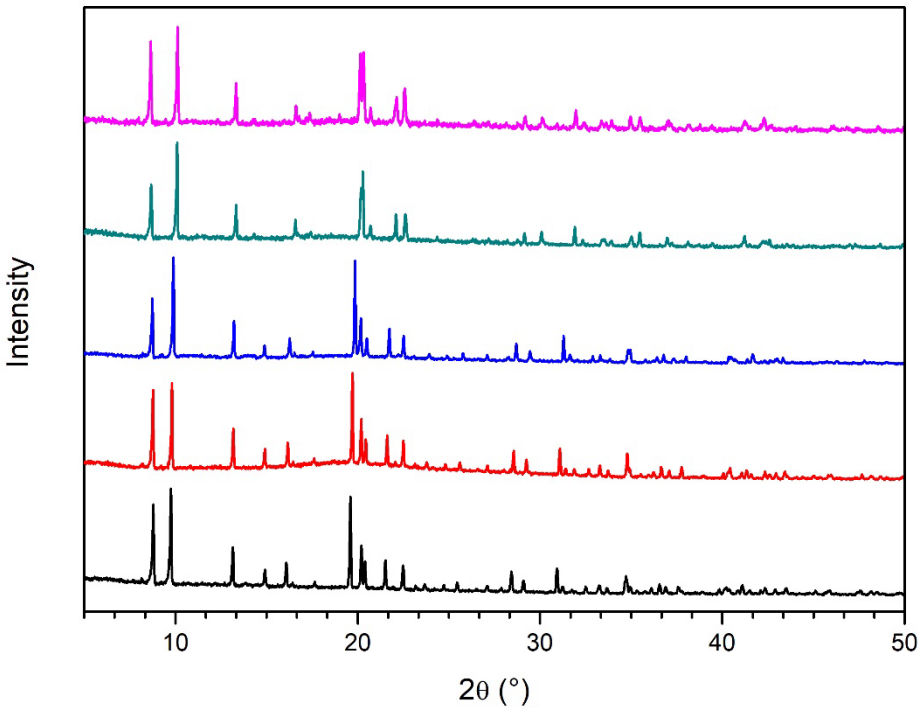

Figure S6. Powder XRD of compounds **1** (black), **2** (red), **3** (blue), **4** (green) and **5** (pink).

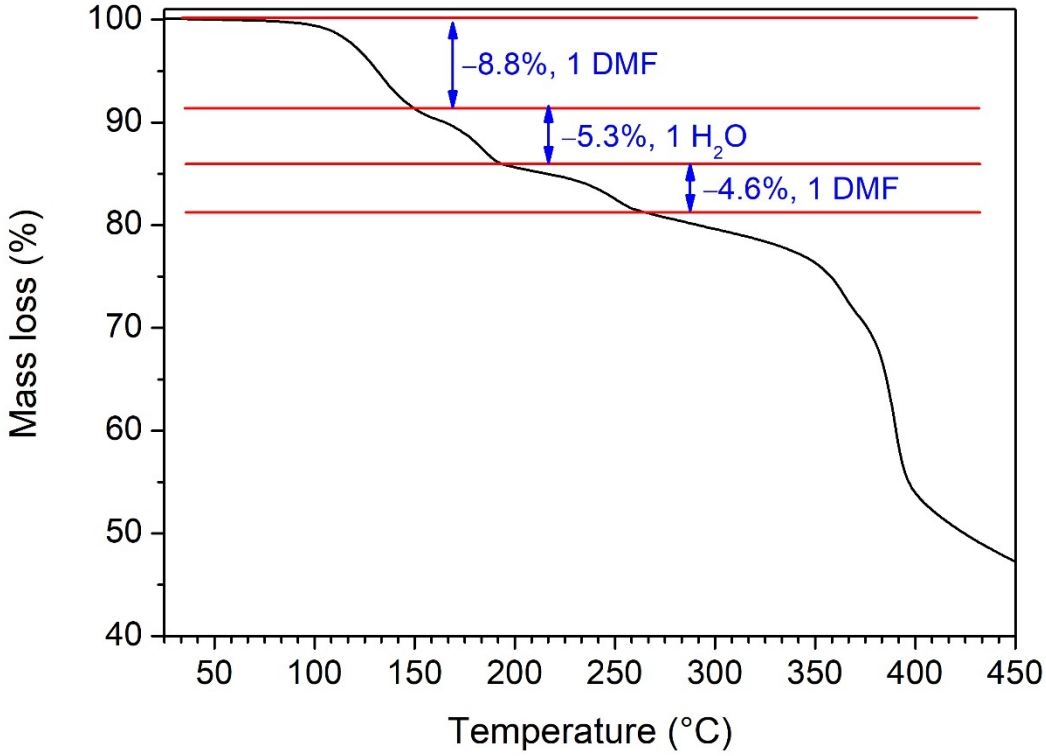

Figure S7. Thermal Gravimetric Analysis (TGA) of compound **3** from 25 to 450 °C.

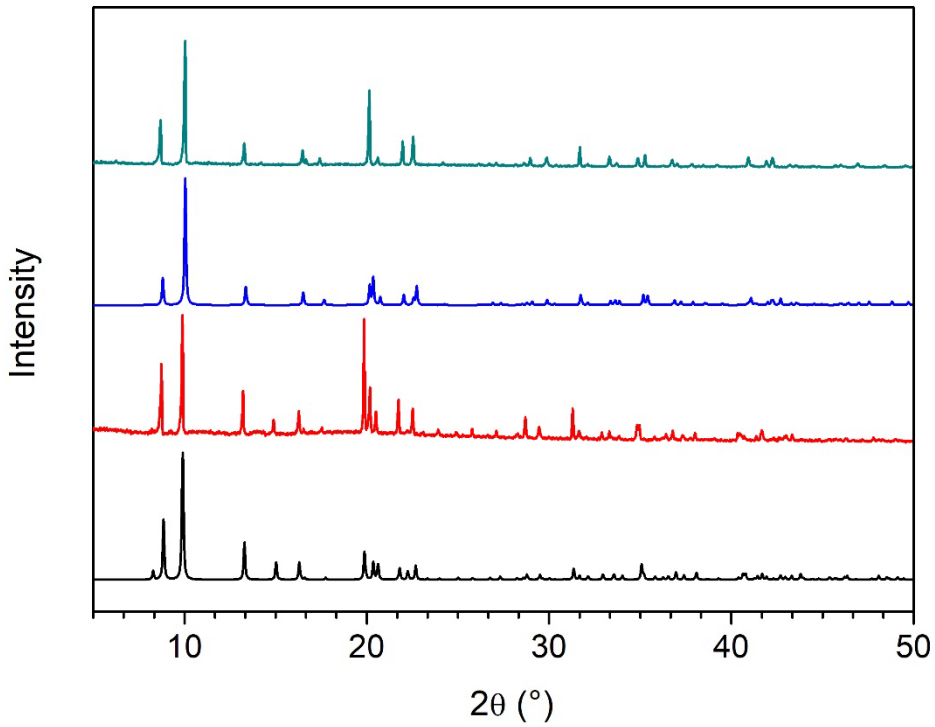

Figure S8. Powder XRD of the single-crystal-to-single-crystal transformation of **3** to **3a**. Compound **3** is shown with the calculated (black) and experimental (red) patterns and compound **3a** with the calculated (blue) and experimental (green) patterns.

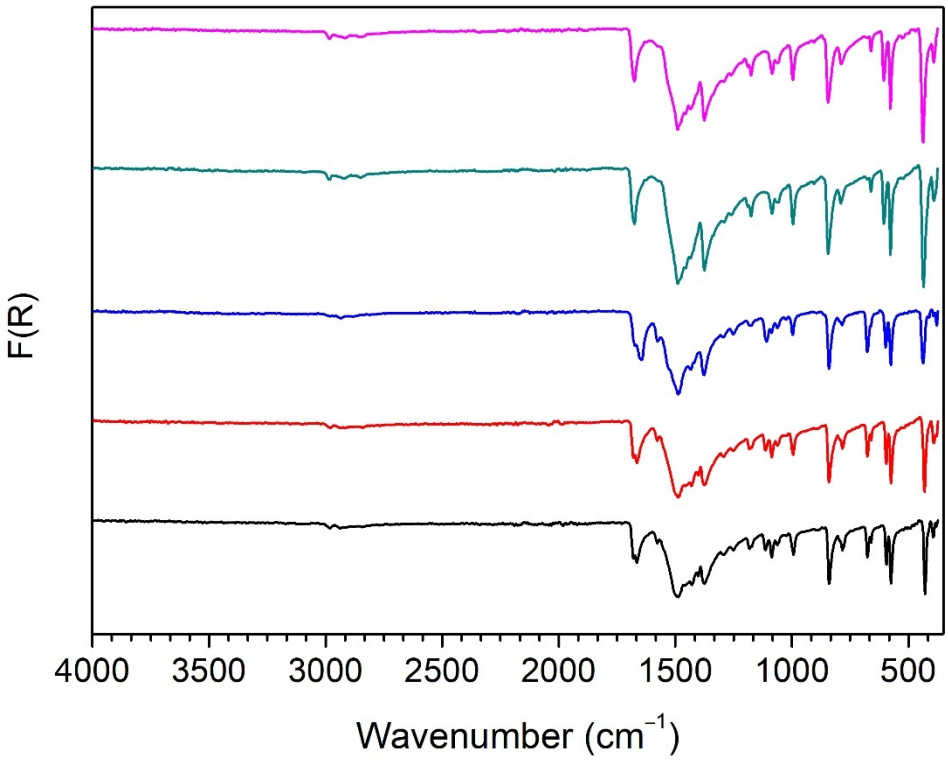

Figure S9. Fourier Transform Infrared (FTIR) spectra of compounds **1** (black), **2** (red), **3** (blue), **4** (green), **5** (pink) from 3000 - 400 cm^{-1}.

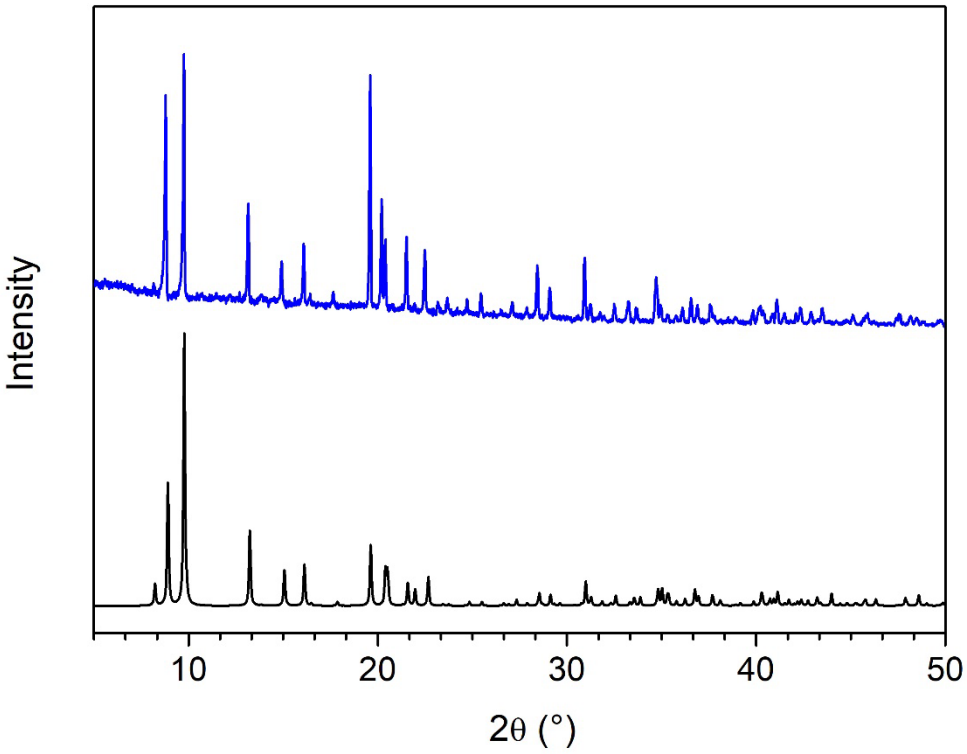

Figure S10. Powder XRD of compound **1** with calculated (black) and experimental (blue) patterns.

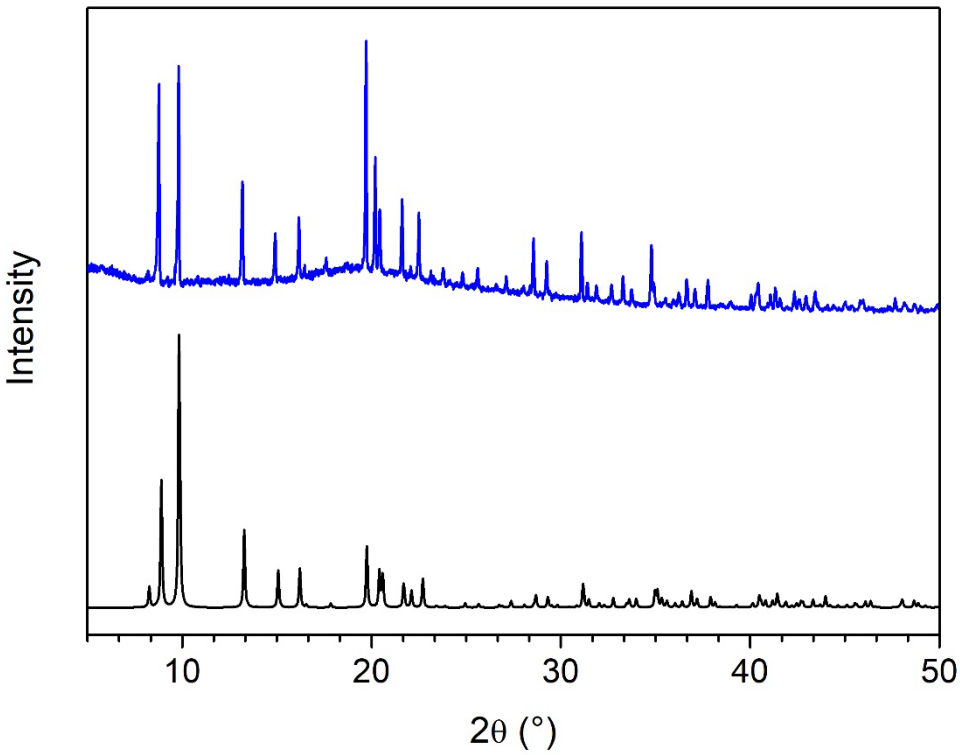

Figure S11. Powder XRD of compound **2** with calculated (black) and experimental (blue) patterns.

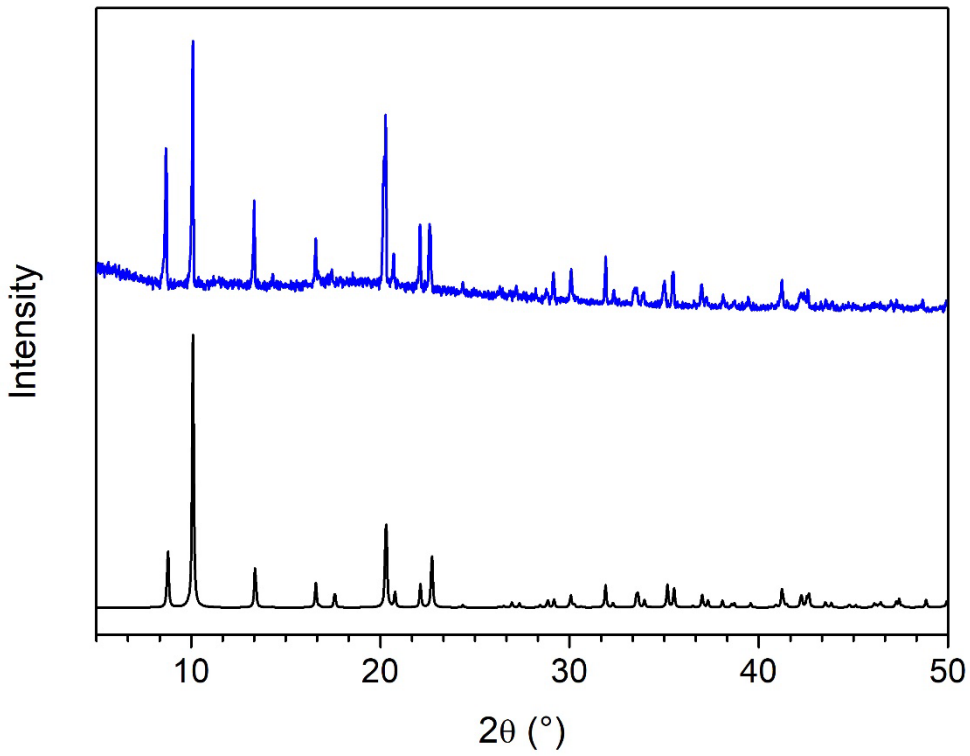

Figure S12. Powder XRD of compound **4** with calculated (black) and experimental (blue) patterns.

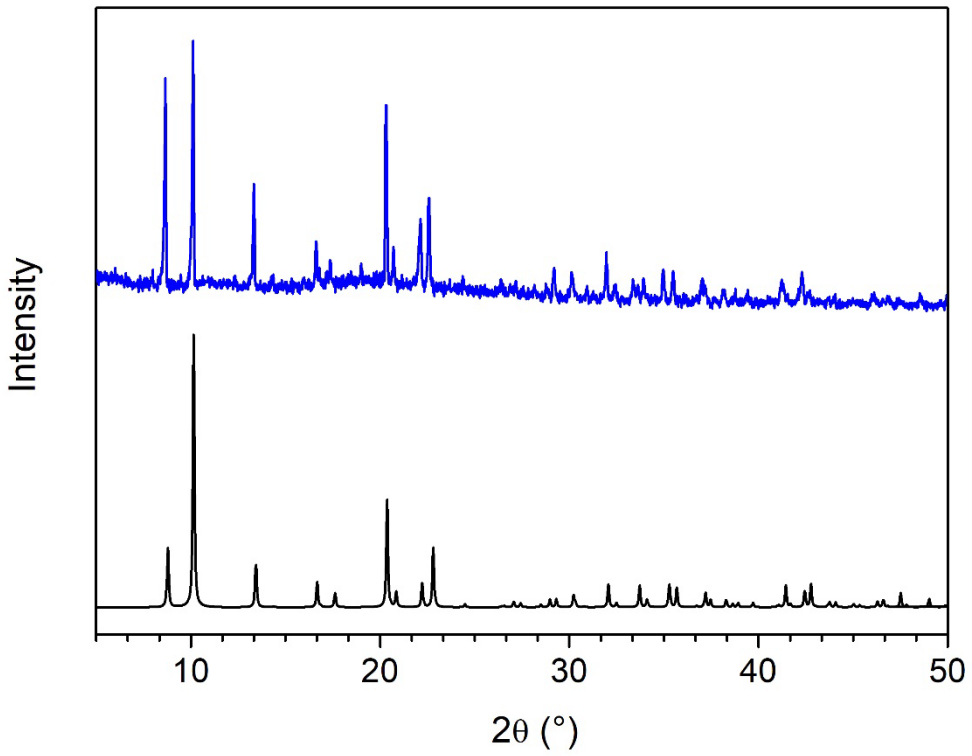

Figure S13. Powder XRD of compound **5** with calculated (black) and experimental (blue) patterns.