SUPPORTING INFORMATION

Halogen influence on the crystal packing of 3,4,5,6-tetra-chloro-phthalate-based lanthanide coordination compounds.

Fallou Ngom[b], Chloé Blais[a], Insa Badiane,[b] Christine Hénaff,[a] Magatte Camara[b], Carole Daiguebonne[a] * and Olivier Guillou[a, c] *

[a] Univ Rennes, INSA Rennes, CNRS UMR 6226 "Institut des Sciences Chimiques de Rennes", 35708 Rennes, France.

[b] Université Assane Seck de Ziguinchor, "Laboratoire de Chimie et de Physique des Matériaux", BP 523 Ziguinchor, Sénégal.

[c] Institut Universitaire de France, 1 rue Descartes, 75005 Paris, France

* To whom correspondence should be addressed.

olivier.guillou@insa-rennes.fr ; carole.daiguebonne@insa-rennes.fr

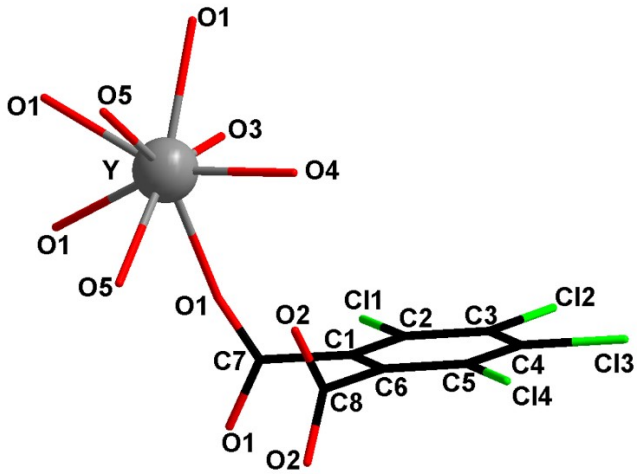

Figure S1. Asymmetric unit of $[Y(tcpa)(OH)(H_2O)_3]_\infty$ **(1.)** with the numbering scheme. H atoms have been omitted for clarity.

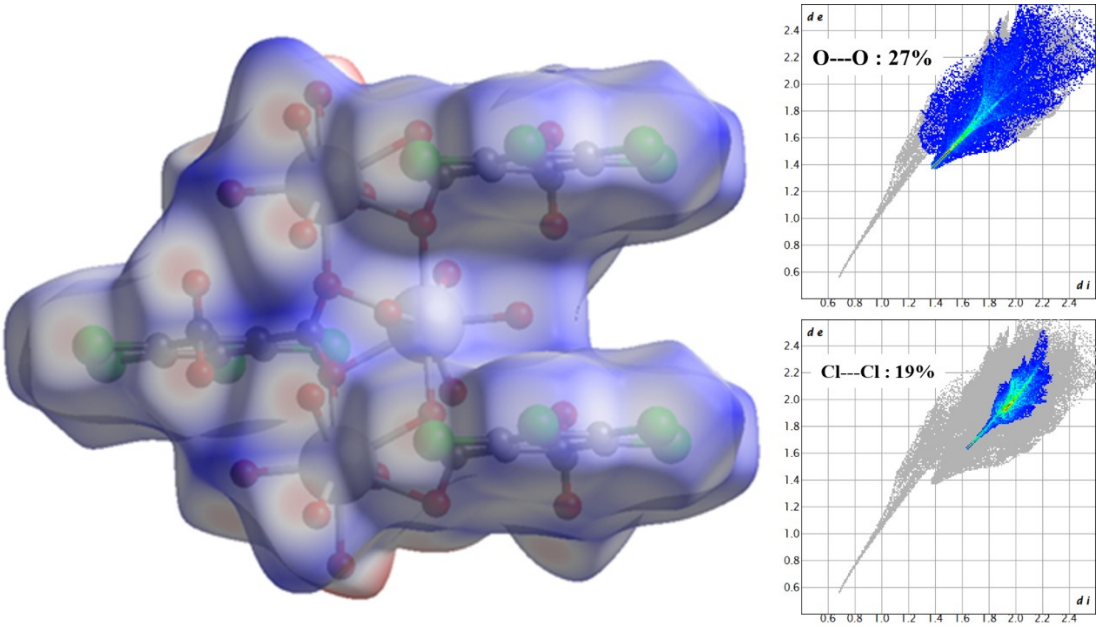

Figure S2. d_{norm} surface (left) and fingerprint plots (right) of the molecular motif of $[Y(tcpa)(OH)(H_2O)_3]_\infty$ **(1.)**.

Table S1. Continuous Shape Measurements (CShM) for $[Y(tcpa)(OH)(H_2O)_3]_\infty$ **(1.)**. The lower is the CShM value, the better is the agreement with the given coordination polyhedron.

$[ML_8]$	OP-8	HPY-8	HBPY-8	CU-8	SAPR-8	TDD-8	JGBF-8	JETBPY-8	JBTPR-8	**BTPR-8**	JSD-8	TT-8	ETBPY-8
Y	30.785	23.560	17.560	13.311	3.225	2.882	14.543	28.746	2.835	**2.209**	4.882	13.893	24.499

OP-8 ≡ D_{8h}-Octagon; HPY-8 ≡ C_{7v}-Heptagonal pyramid; HBPY-8 ≡ D_{6h}-Hexagonal bipyramid; CU-8 ≡ O_h-Cube; SAPR-8 ≡ D_{4d}-Square antiprism; TDD-8 ≡ D_{2d}-Triangular dodecahedron; JGBF-8 ≡ D_{2d}-Johnson gyrobifastigium J26; JETBPY-8 ≡ D_{3h}-Johnson elongated triangular bipyramid J14; JBTPR-8 ≡ C_{2v}-Biaugmented trigonal prism J50; **BTPR-8 ≡ C_{2v}-Biaugmented trigonal prism**; JSD-8 ≡ D_{2d}-Snub diphenoid J84; TT-8 ≡ T_d-Triakis tetrahedron; ETBPY-8 ≡ D_{3h}-Elongated trigonal bipyramid.

Table S2. Cl-Cl distances shorter than 3.5 Å in $[Y(tcpa)(OH)(H_2O)_3]_\infty$ **(1.)**.

Atom1	Atom2	Symmetry code of Atom2	Distance (Å)
Cl4	Cl3	x, y, z	3.1016
	Cl1	-1+x, y, z	3.2798
Cl3	Cl4	x, y, z	3.1016
	Cl2	x, y, z	3.1323
Cl2	Cl1	x, y, z	3.1185
	Cl3	x, y, z	3.1323
Cl1	Cl2	x, y, z	3.1185
	Cl4	1+x, y, z	3.2798

Table S3. O-O distances shorter than 3.0 Å in $[Y(tcpa)(OH)(H_2O)_3]_\infty$ **(1.)**.

Atom1	Atom2	Symmetry code of Atom2	Distance (Å)
O2	O2	x, 0.5-y, z	2.1964
	O5	-x, 1-y, 2-z	2.7459
	O4	x, y, z	2.7684
O1	O1	x, 0.5-y, z	2.1570
	O3	x, y, z	2.8381
	O1	1-x, 1-y, 2-z	2.9082
	O5	x, y, z	2.9388
O3	O5	1-x, 0.5+y, 2-z	2.7612
	O5	1-x, 1-y, 2-z	2.7612
	O1	x, 1.5-y, z	2.8381
	O1	x, y, z	2.8381
O4	O2	x, y, z	2.7684
	O2	x, 1.5-y, z	2.7684
O5	O2	-x, 1-y, 2-z	2.7459
	O3	1-x, -0.5+y, 2-z	2.7612
	O5	x, 1.5-y, z	2.8593
	O1	x, y, z	2.9388

Table S4. Continuous Shape Measurements (CShM) for $Nd_4(tcpa)_6(H_2O)_{22}\cdot 8H_2O$ **(2.)**. The lower is the CShM value, the better is the agreement with the given coordination polyhedron.

[ML_9]	EP-9	OPY-9	HBPY-9	JTC-9	JCCU-9	CCU-9	JCSAPR-9	**CSAPR-9**	JTCTPR-9	TCTPR-9	JTDIC-9	HH-9	**MFF-9**
Nd1	35.983	23.060	18.251	15.275	10.731	9.045	2.095	1.323	2.680	1.386	13.132	9.021	**0.988**
Nd2	36.111	21.890	18.594	16.827	10.943	9.629	1.962	**0.864**	3.264	1.031	12.697	10.459	0.916

EP-9 ≡ D_{9h}-Enneagon; OPY-9 ≡ C_{8v}-Octagonal pyramid; HBPY-9 ≡ D_{7h}-Heptagonal bipyramid; JTC-9 ≡ C_{3v}-Johnson triangular cupola J3; JCCU-9 ≡ C_{4v}-Capped cube J8; CCU-9 ≡ C_{4v}-Spherical-relaxed capped cube; JCSAPR-9 ≡ $_{C4v}$-Capped square antiprism J10; **CSAPR-9 ≡ C_{4v}-Spherical capped square antiprism**; JTCTPR-9 ≡ D_{3h}-Tricapped trigonal prism J51; TCTPR-9 ≡ D_{3h}-Spherical tricapped trigonal prism; JTDIC-9 ≡ C_{3v}-Tridiminished icosahedron J63; HH-9 ≡ C_{2v}-Hula-hoop; **MFF-9 ≡ C_s-Muffin**.

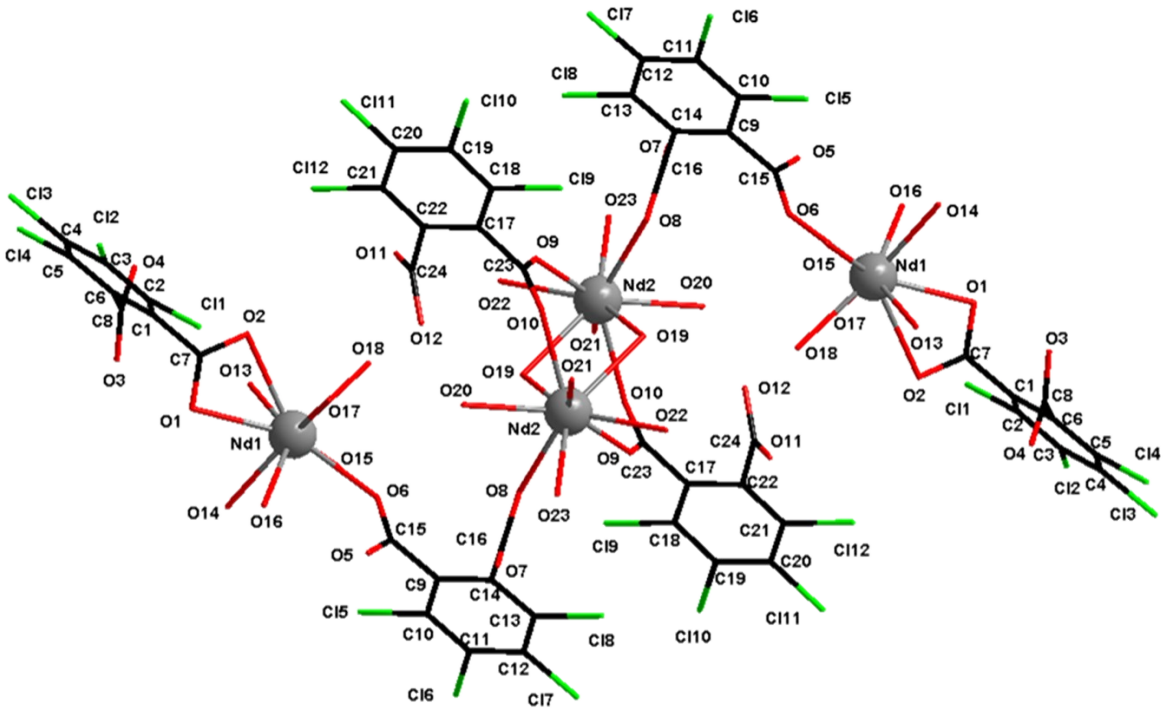

Figure S3. Projection view of the tetranuclear molecular motif of $[Nd_4(tcpa)_6(H_2O)_{22}\cdot 8H_2O$ **(2.)** with the numbering scheme.

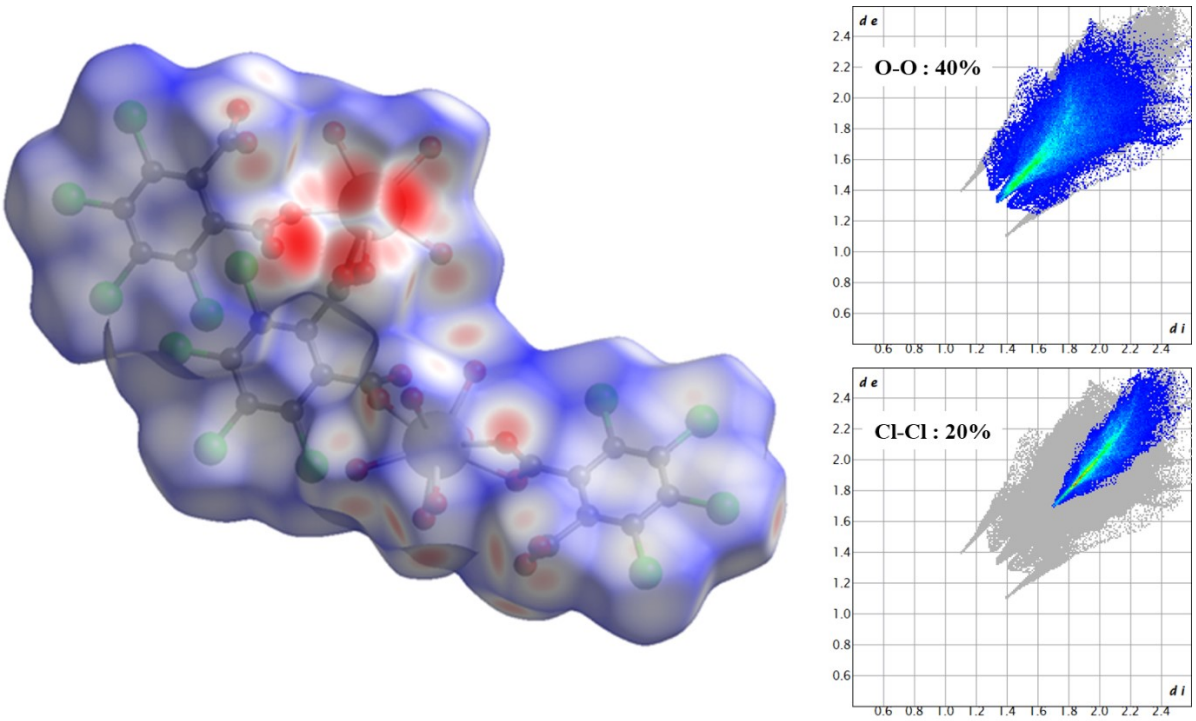

Figure S4. d_{norm} surface (left) and fingerprint plots (right) of the molecular motif of $[Nd_4(tcpa)_6(H_2O)_{22}\cdot 8H_2O$ **(2.)**.

Table S5. O-O distances shorter than 3.0 Å in $Nd_4(tcpa)_6(H_2O)_{22}\cdot 8H_2O$ **(2.)**.

Atom1	Atom2	Symmetry code of Atom2	Distance (Å)
O19	OW4	x, y, z	2.6573
	O9	1-x, 1-y, 1-z	2.7790
	O10	x, y, z	2.8311
	O12	1-x, 1-y, 1-z	2.8415
	O8	x, y, z	2.8813
	O22	1-x, 1-y, 1-z	2.9836
	O10	1-x, 1-y, 1-z	2.9873
O20	O7	2-x, 1-y, 1-z	2.6936
	O12	1-x, 1-y, 1-z	2.7626
	O10	1-x, 1-y, 1-z	2.8720
O22	O3	x, y, -1+z	2.7705
	O9	x, y, z	2.7727
	O21	x, y, z	2.8614
	O11	x, y, z	2.9408
	O19	1-x, 1-y, 1-z	2.9836
	O23	x, y, z	2.9910
O8	O9	x, y, z	2.7721
	O19	x, y, z	2.8813
	O23	x, y, z	2.8902
O1	O14	2-x, 1-y, 2-z	2.7603
	O16	x, y, z	2.9206
O10	O21	1-x, 1-y, 1-z	2.7007
	O19	x, y, z	2.8311
	O20	1-x, 1-y, 1-z	2.8720
	O19	1-x, 1-y, 1-z	2.9873
O17	OW3	x, y, z	2.7634
	O12	1-x, 1-y, 1-z	2.7981
	O16	x, y, z	2.8792
	O18	x, y, z	2.9559
	O2	x, y, z	2.9623
O6	O15	x, y, z	2.7669
	O16	x, y, z	2.9503
	OW4	x, y, z	2.9805
O9	O8	x, y, z	2.7721
	O22	x, y, z	2.7727
	O19	1-x, 1-y, 1-z	2.7790
OW4	O19	x, y, z	2.6573
	O4	1-x, 1-y, 2-z	2.8441
	O6	x, y, z	2.9805
OW2	O2	x, y, z	2.6586
	O13	1-x, 1-y, 2-z	2.6876
	O15	1-x, 1-y, 2-z	2.8155
	O11	1-x, 1-y, 1-z	2.8785
O23	O7	x, y, z	2.5760
	O21	x, y, z	2.8002

	O5	2-x, 1-y, 1-z	2.8212
	OW3	2-x, 1-y, 1-z	2.8595
	O8	x, y, z	2.8902
	O22	x, y, z	2.9910
O18	O4	1-x, 1-y, 2-z	2.7272
	O11	1-x, 1-y, 1-z	2.9524
	O17	x, y, z	2.9559
	O15	x, y, z	2.9876
O12	O20	1-x, 1-y, 1-z	2.7626
	O17	1-x, 1-y, 1-z	2.7981
	O19	1-x, 1-y, 1-z	2.8415
O5	O16	x, y, z	2.7092
	O23	2-x, 1-y, 1-z	2.8212
	O21	2-x, 1-y, 1-z	2.8239
O2	OW2	x, y, z	2.6586
	O13	x, y, z	2.7272
	O17	x, y, z	2.9623
O16	O5	x, y, z	2.7092
	O3	2-x, 1-y, 2-z	2.8520
	O17	x, y, z	2.8792
	O14	x, y, z	2.8879
	O1	x, y, z	2.9206
	O6	x, y, z	2.9503
OW1	O14	x, y, z	2.7350
	OW3	2-x, 1-y, 2-z	2.8568
	O11	x, y, 1+z	2.9624
O14	OW1	x, y, z	2.7350
	O1	2-x, 1-y, 2-z	2.7603
	O16	x, y, z	2.8879
	O15	x, y, z	2.9603
O11	OW2	1-x, 1-y, 1-z	2.8785
	O22	x, y, z	2.9408
	O18	1-x, 1-y, 1-z	2.9524
	OW1	x, y, -1+z	2.9624
O21	O10	1-x, 1-y, 1-z	2.7007
	O23	x, y, z	2.8002
	O5	2-x, 1-y, 1-z	2.8239
	O22	x, y, z	2.8614
O7	O23	x, y, z	2.5760
	O20	2-x, 1-y, 1-z	2.6936
O15	O6	x, y, z	2.7669
	OW2	1-x, 1-y, 2-z	2.8155
	O13	x, y, z	2.8331
	O4	1-x, 1-y, 2-z	2.9296
	O14	x, y, z	2.9603
	O18	x, y, z	2.9876
OW3	O17	x, y, z	2.7634
	OW1	2-x, 1-y, 2-z	2.8568
	O23	2-x, 1-y, 1-z	2.8595
O13	OW2	1-x, 1-y, 2-z	2.6876

	O2	x, y, z	2.7272
	O15	x, y, z	2.8331
O3	O22	x, y, 1+z	2.7705
	O16	2-x, 1-y, 2-z	2.8520
O4	O18	1-x, 1-y, 2-z	2.7272
	OW4	1-x, 1-y, 2-z	2.8441
	O15	1-x, 1-y, 2-z	2.9296

Table S6. Cl-Cl distances shorter than 3.5 Å in $Nd_4(tcpa)_6(H_2O)_{22}\cdot 8H_2O$ **(2.)**.

Atom1	Atom2	Symmetry code of Atom2	Distance (Å)
Cl4	Cl2	1-x, 2-y, 2-z	3.4400
Cl8	Cl7	2-x, -y, 1-z	3.4036
	Cl8	2-x, -y, 1-z	3.5060
Cl7	Cl8	2-x, -y, 1-z	3.4036
Cl10	Cl1	x, -1+y, z	3.4900
Cl1	Cl10	x, 1+y, z	3.4900
Cl2	Cl4	1-x, 2-y, 2-z	3.4400

Table S7. Continuous Shape Measurements (CShM) for $[KLa(tcpa)_2(H_2O)_{10}\cdot H_2O]_\infty$ **(3.)**. The lower is the CShM value, the better is the agreement with the given coordination polyhedron.

[ML_9]	EP-9	OPY-9	HBPY-9	JTC-9	JCCU-9	CCU-9	JCSAPR-9	**CSAPR-9**	JTCTPR-9	TCTPR-9	JTDIC-9	HH-9	MFF-9
La	36.246	20.385	19.619	16.227	10.766	9.627	1.871	**0.861**	2.726	0.989	12.758	11.070	1.435

EP-9 ≡ D_{9h}-Enneagon; OPY-9 ≡ C_{8v}-Octagonal pyramid; HBPY-9 ≡ D_{7h}-Heptagonal bipyramid; JTC-9 ≡ C_{3v}-Johnson triangular cupola J3; JCCU-9 ≡ C_{4v}-Capped cube J8; CCU-9 ≡ C_{4v}-Spherical-relaxed capped cube; JCSAPR-9 ≡ $_{C4v}$-Capped square antiprism J10; **CSAPR-9 ≡ C_{4v}-Spherical capped square antiprism**; JTCTPR-9 ≡ D_{3h}-Tricapped trigonal prism J51; TCTPR-9 ≡ D_{3h}-Spherical tricapped trigonal prism; JTDIC-9 ≡ C_{3v}-Tridiminished icosahedron J63; HH-9 ≡ C_{2v}-Hula-hoop; MFF-9 ≡ C_s-Muffin.

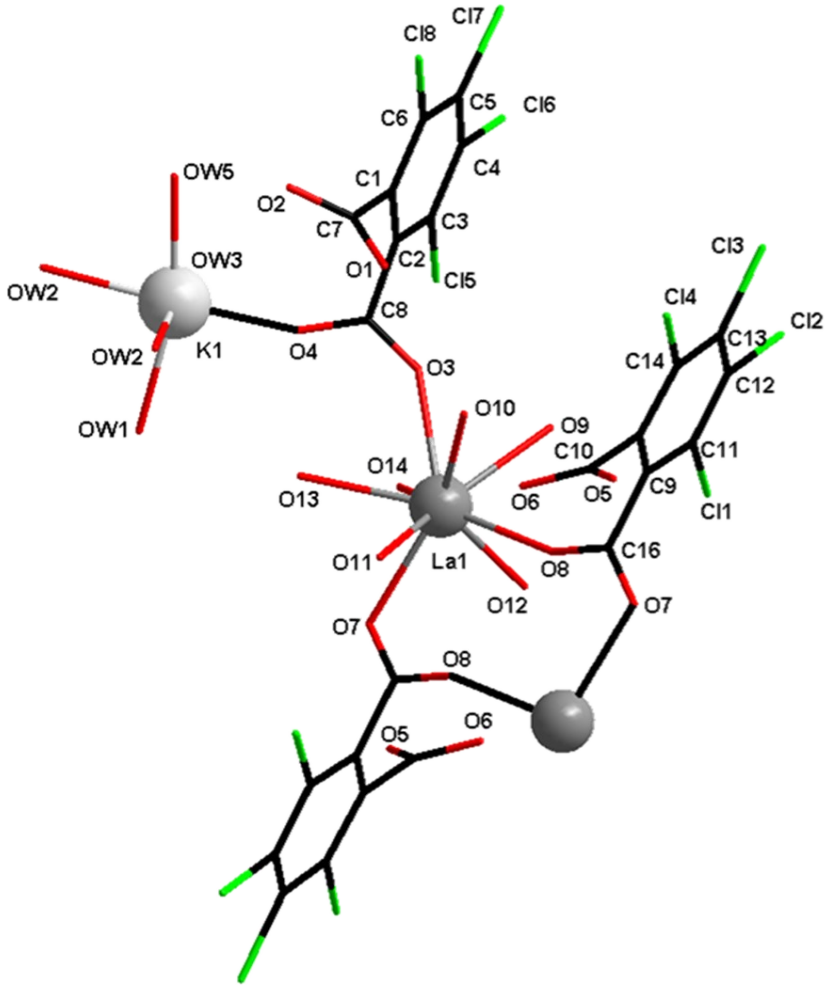

Figure S5. Extended asymmetric unit of $[KLa(tcpa)_2(H_2O)_{10}\cdot H_2O]_\infty$ **(3.)** with the numbering scheme. Hydrogen atoms have been omitted for clarity. K is in light grey and La in dark grey.

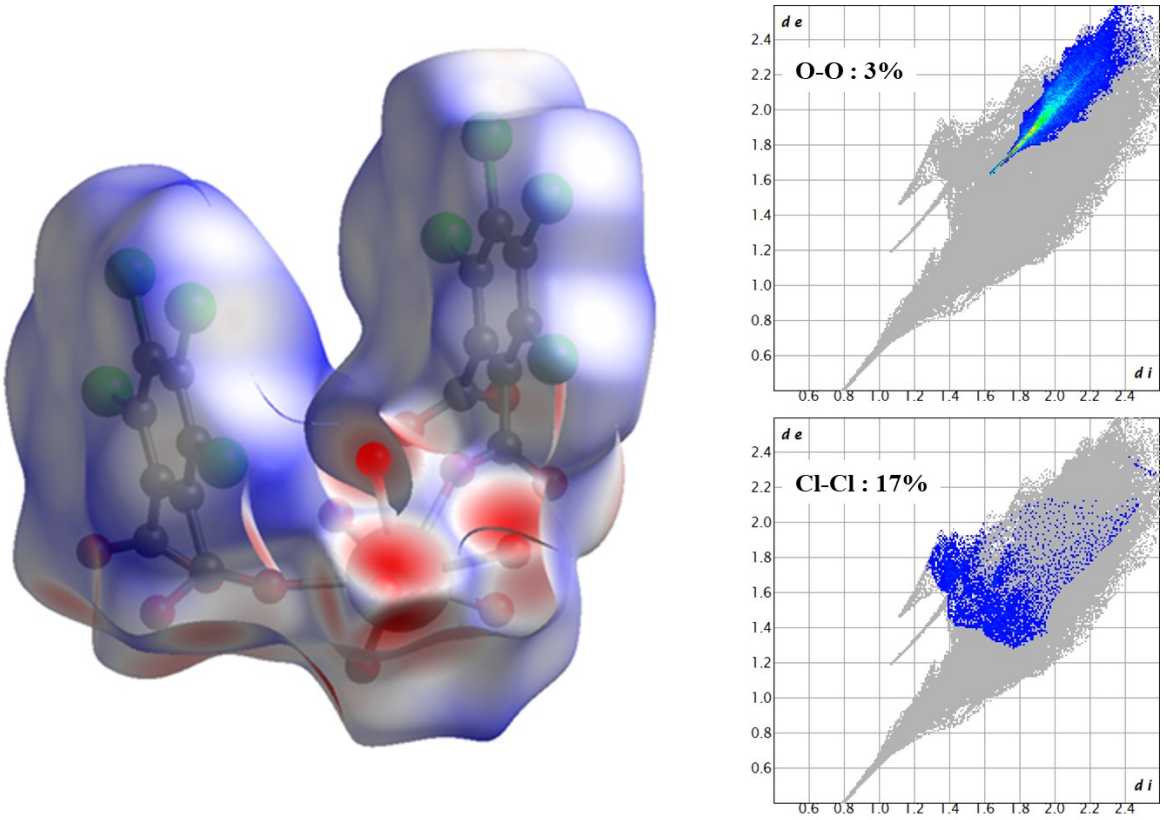

Figure S6. d_{norm} surface (left) and fingerprint plots (right) of the molecular motif of $[KLa(tcpa)_2(H_2O)_{10}\cdot H_2O]_\infty$ **(3.)**.

Table S8. Cl-Cl distances shorter than 3.5 Å in $[KLa(tcpa)_2(H_2O)_{10}\cdot H_2O]_\infty$ **(3.)**.

Atom1	Atom2	Symmetry code of Atom2	Distance (Å)
Cl1	Cl4	1+x, y, z	3.3767
	Cl2	2-x, 1-y, 1-z	3.5177
Cl6	Cl5	2-x, 1-y, -z	3.4375
Cl8	Cl4	-x, 1-y, 1-z	3.2779
Cl5	Cl6	2-x, 1-y, -z	3.4375
Cl2	Cl2	2-x, 1-y, 1-z	3.4339
	Cl1	2-x, 1-y, 1-z	3.5177
Cl4	Cl8	-x, 1-y, 1-z	3.2779
	Cl1	-1+x, y, z	3.3767

Table S9. O-O distances shorter than 3.0 Å in $[KLa(tcpa)_2(H_2O)_{10}\cdot H_2O]_\infty$ **(3.)**.

Atom1	Atom2	Symmetry code of Atom2	Distance (Å)
O12	O1	1+x, y, z	2.7005
	O11	2-x, -y, 1-z	2.7702
	O6	2-x, -y, 1-z	2.9200
	O14	x, y, z	2.9224
	O9	x, y, z	2.9283
	O7	2-x, -y, 1-z	2.9737
O8	O7	x, y, z	2.2058
	O11	2-x, -y, 1-z	2.8679
	O8	2-x, -y, 1-z	2.9460
	O10	x, y, z	2.9767
O14	O2	1+x, y, z	2.6713
	OW1	2-x, -y, -z	2.8061
	OW2	2-x, -y, -z	2.8263
	O3	x, y, z	2.8812
	O12	x, y, z	2.9224
	O7	2-x, -y, 1-z	2.9820
O6	O5	x, y, z	2.2265
	O11	1-x, -y, 1-z	2.7723
	O10	x, y, z	2.7978
	O12	2-x, -y, 1-z	2.9200
O7	O8	x, y, z	2.2058
	OW3	x, y, 1+z	2.9170
	O12	2-x, -y, 1-z	2.9737
	O14	2-x, -y, 1-z	2.9820
O13	O4	x, y, z	2.6883
	O11	x, y, z	2.7774
	O3	x, y, z	2.8990
	O5	1-x, -y, 1-z	2.9879
O3	O4	x, y, z	2.2349
	O9	x, y, z	2.6208
	O10	x, y, z	2.6935

	O14	x, y, z	2.8812
	O13	x, y, z	2.8990
O9	O3	x, y, z	2.6208
	O12	x, y, z	2.9283
O11	O12	2-x, -y, 1-z	2.7702
	O6	1-x, -y, 1-z	2.7723
	O13	x, y, z	2.7774
	O8	2-x, -y, 1-z	2.8679
	O10	x, y, z	2.9464
O1	O2	x, y, z	2.2348
	O12	-1+x, y, z	2.7005
OW2	O14	2-x, -y, -z	2.8263
	O5	x, y, -1+z	2.8915
	OW5	x, y, z	2.9774
O5	O6	x, y, z	2.2265
	OW4	-1+x, y, 1+z	2.8118
	OW2	x, y, 1+z	2.8915
	O13	1-x, -y, 1-z	2.9879
O2	O1	x, y, z	2.2348
	O14	-1+x, y, z	2.6713
	OW5	x, y, z	2.7291
O4	O3	x, y, z	2.2349
	O13	x, y, z	2.6883
OW1	O14	2-x, -y, -z	2.8061
	OW5	1-x, -y, -z	2.9058
OW5	O2	x, y, z	2.7291
	OW1	1-x, -y, -z	2.9058
	OW2	x, y, z	2.9774
O10	O3	x, y, z	2.6935
	O6	x, y, z	2.7978
	O11	x, y, z	2.9464
	O8	x, y, z	2.9767
OW3	OW4	x, y, z	2.7381
	O7	x, y, -1+z	2.9170
OW4	OW3	x, y, z	2.7381
	O5	1+x, y, -1+z	2.8117

Table S10. Continuous Shape Measurements (CShM) for $[KLa(tcpa)_2(H_2O)_5 \cdot 2H_2O]_\infty$ **(4.)**. The lower is the CShM value, the better is the agreement with the given coordination polyhedron.

[ML_9]	EP-9	OPY-9	HBPY-9	JTC-9	JCCU-9	CCU-9	JCSAPR-9	**CSAPR-9**	JTCTPR-9	TCTPR-9	JTDIC-9	HH-9	MFF-9
La	32.952	22.803	17.011	13.883	9.159	7.736	2.236	**1.449**	2.483	1.783	12.438	9.254	1.680

EP-9 ≡ D_{9h}-Enneagon; OPY-9 ≡ C_{8v}-Octagonal pyramid; HBPY-9 ≡ D_{7h}-Heptagonal bipyramid; JTC-9 ≡ C_{3v}-Johnson triangular cupola J3; JCCU-9 ≡ C_{4v}-Capped cube J8; CCU-9 ≡ C_{4v}-Spherical-relaxed capped cube; JCSAPR-9 ≡ $_{C4v}$-Capped square antiprism J10; **CSAPR-9 ≡ C_{4v}-Spherical capped square antiprism**; JTCTPR-9 ≡ D_{3h}-Tricapped trigonal prism J51; TCTPR-9 ≡ D_{3h}-Spherical tricapped trigonal prism; JTDIC-9 ≡ C_{3v}-Tridiminished icosahedron J63; HH-9 ≡ C_{2v}-Hula-hoop; MFF-9 ≡ C_s-Muffin.

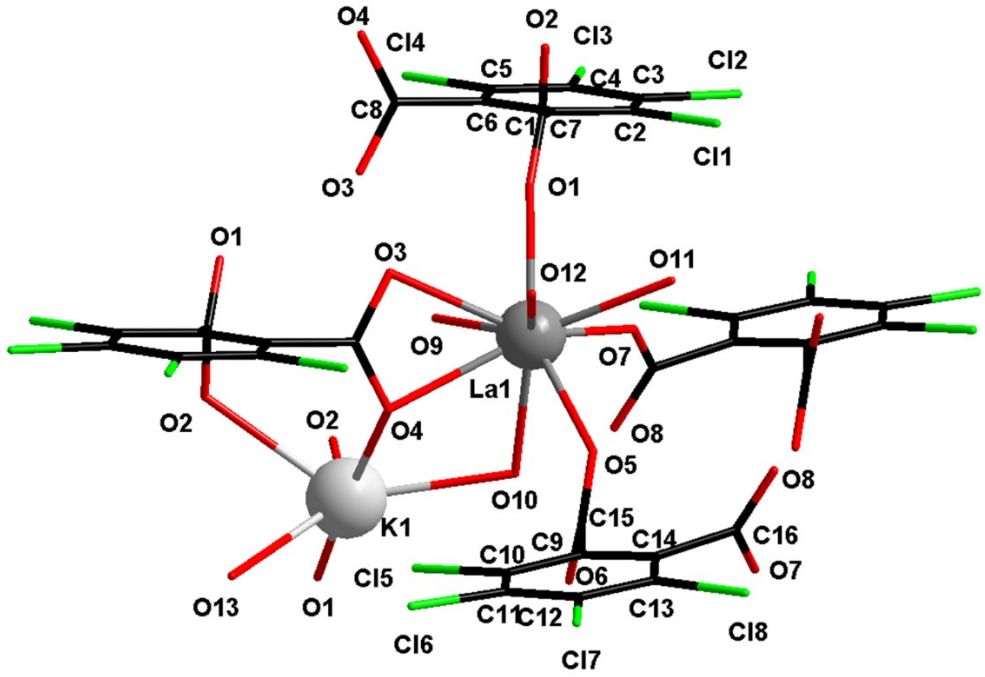

Figure S7. Extended asymmetric unit of $[KLa(tcpa)_2(H_2O)_5{\cdot}2H_2O]_\infty$ **(4.)** with the numbering scheme. Hydrogen atoms have been omitted for clarity. K is in light grey and La in dark grey.

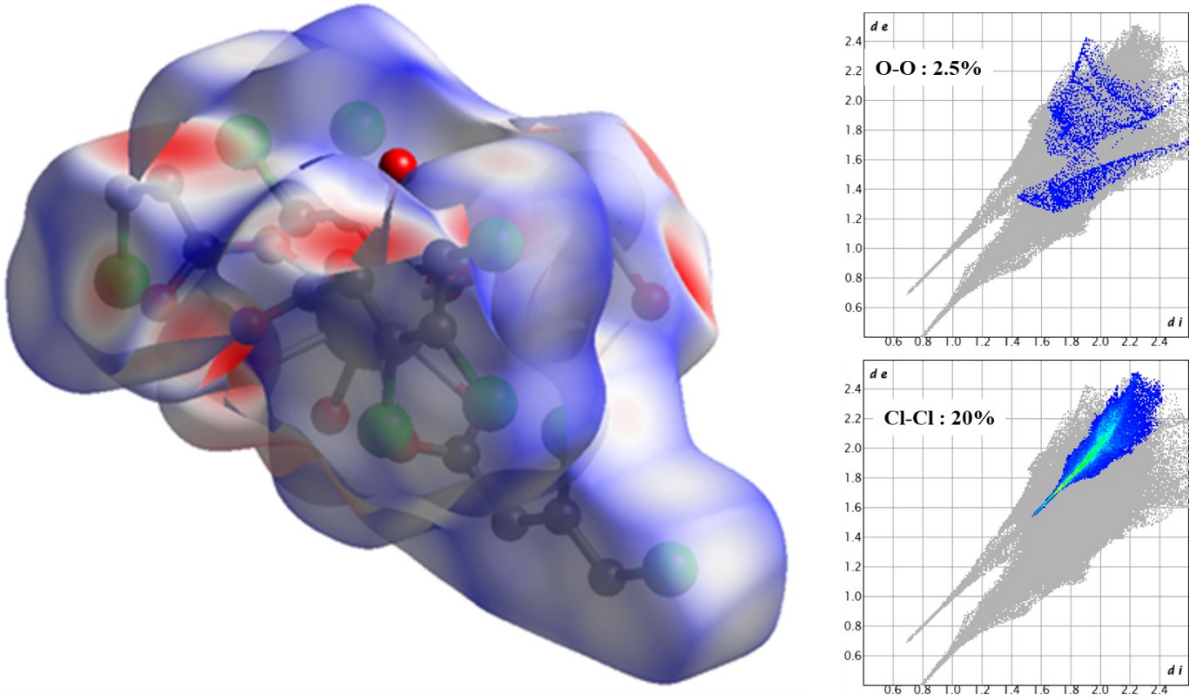

Figure S8. d_{norm} surface (left) and fingerprint plots (right) of the molecular motif of $[KLa(tcpa)_2(H_2O)_5{\cdot}2H_2O]_\infty$ **(4.)**.

Table S11. O-O distances shorter than 3.0 Å in $[KLa(tcpa)_2(H_2O)_5 \cdot 2H_2O]_\infty$ **(4.)**.

Atom1	Atom2	Symmetry code of Atom2	Distance (Å)
O1	O2	x, y, z	2.2143
	O3	1-x, -y, 1-z	2.9023
O2	O1	x, y, z	2.2143
	OW2	-1+x, y, z	2.6820
O3	O4	x, y, z	2.2037
	O9	x, y, z	2.6962
	O12	1-x, -y, 1-z	2.8856
	O1	1-x, -y, 1-z	2.9023
	O9	1-x, -y, 1-z	2.9911
O4	O3	x, y, z	2.2037
O5	O6	x, y, z	2.2293
	O10	x, y, z	2.9573
	O12	x, y, z	2.9752
O6	O5	x, y, z	2.2293
	O10	x, y, z	2.7386
	OW1	1+x, y, z	2.7739
	O11	1-x, 1-y, 1-z	2.8161
O7	O8	x, y, z	2.2327
	O11	1-x, 1-y, 1-z	2.8920
O8	O7	x, y, z	2.2327
	O10	1-x, 1-y, 1-z	2.6953
	OW1	x, y, z	2.7949
O9	O3	x, y, z	2.6962
	OW2	x, y, z	2.7348
	O10	x, y, z	2.8832
	O3	1-x, -y, 1-z	2.9911
O10	O8	1-x, 1-y, 1-z	2.6953
	O6	x, y, z	2.7386
	O9	x, y, z	2.8832
	O5	x, y, z	2.9573
O11	OW1	x, y, z	2.7792
	O12	x, y, z	2.7964
	O6	1-x, 1-y, 1-z	2.8161
	O7	1-x, 1-y, 1-z	2.8920
O12	OW1	x, y, z	2.7506
	O13	x, y, z	2.7540
	O11	x, y, z	2.7964
	O3	1-x, -y, 1-z	2.8856
	O5	x, y, z	2.9752
O13	O12	x, y, z	2.7540
	OW2	1-x, -y, 1-z	2.8166
OW1	O12	x, y, z	2.7506
	O6	-1+x, y, z	2.7739
	O11	x, y, z	2.7792
	O8	x, y, z	2.7949
OW2	O2	1+x, y, z	2.6820
	O9	x, y, z	2.7348
	O13	1-x, -y, 1-z	2.8166

Table S12. Cl-Cl distances shorter than 3.5 Å in $[KLa(tcpa)_2(H_2O)_5 \cdot 2H_2O]_\infty$ **(4.)**.

Atom1	Atom2	Symmetry code of Atom2	Distance (Å)
Cl1	Cl2	x, y, z	3.1250
Cl2	Cl1	x, y, z	3.1250
	Cl3	x, y, z	3.1254
	Cl5	-1+x, y, 1+z	3.3870
	Cl6	-1+x, y, 1+z	3.4414
Cl3	Cl4	x, y, z	3.1028
	Cl2	x, y, z	3.1254
Cl4	Cl3	x, y, z	3.1028
	Cl7	x, -1+y, 1+z	3.2991
	Cl8	x, -1+y, 1+z	3.3871
Cl5	Cl6	x, y, z	3.1319
	Cl2	1+x, y, -1+z	3.3870
Cl6	Cl7	x, y, z	3.1039
	Cl5	x, y, z	3.1319
	Cl2	1+x, y, -1+z	3.4414
Cl7	Cl6	x, y, z	3.1039
	Cl8	x, y, z	3.1090
	Cl4	x, 1+y, -1+z	3.2991
Cl8	Cl7	x, y, z	3.1090
	Cl4	x, 1+y, -1+z	3.3871

Table S13. Continuous Shape Measurements (CShM) for Y(tcpa)(Htcpa)$(H_2O)_5$ **(5.)**. The lower is the CShM value, the better is the agreement with the given coordination polyhedron.

[ML_9]	EP-9	OPY-9	HBPY-9	JTC-9	JCCU-9	CCU-9	JCSAPR-9	CSAPR-9	JTCTPR-9	TCTPR-9	JTDIC-9	HH-9	**MFF-9**
Y	36.208	21.802	17.476	15.687	10.235	8.733	2.150	1.796	3.975	2.600	12.234	8.731	**1.634**

EP-9 ≡ D_{9h}-Enneagon; OPY-9 ≡ C_{8v}-Octagonal pyramid; HBPY-9 ≡ D_{7h}-Heptagonal bipyramid; JTC-9 ≡ C_{3v}-Johnson triangular cupola J3; JCCU-9 ≡ C_{4v}-Capped cube J8; CCU-9 ≡ C_{4v}-Spherical-relaxed capped cube; JCSAPR-9 ≡ $_{C4v}$-Capped square antiprism J10; CSAPR-9 ≡ C_{4v}-Spherical capped square antiprism; JTCTPR-9 ≡ D_{3h}-Tricapped trigonal prism J51; TCTPR-9 ≡ D_{3h}-Spherical tricapped trigonal prism; JTDIC-9 ≡ C_{3v}-Tridiminished icosahedron J63; HH-9 ≡ C_{2v}-Hula-hoop; **MFF-9 ≡ C_s-Muffin**.

Table S14. Cl-Cl distances shorter than 3.5 Å in Y(tcpa)(Htcpa)$(H_2O)_5$ **(5.)**.

Atom1	Atom2	Symmetry code of Atom2	Distance (Å)
Cl5	Cl6	x, y, z	3.0980
	Cl8	0.5-x, y, 0.5+z	3.4866
Cl6	Cl5	x, y, z	3.0980
	Cl7	x, y, z	3.1028
	Cl3	x, -1+y, z	3.4307
Cl1	Cl2	x, y, z	3.1069
Cl7	Cl6	x, y, z	3.1028
	Cl8	x, y, z	3.1063
Cl4	Cl3	x, y, z	3.0882
Cl8	Cl7	x, y, z	3.1063
	Cl5	0.5-x, y, -0.5+z	3.4866
Cl2	Cl1	x, y, z	3.1069
	Cl3	x, y, z	3.1080
Cl3	Cl4	x, y, z	3.0882
	Cl2	x, y, z	3.1080
	Cl6	x, 1+y, z	3.4307

Table S15. O-O distances shorter than 3.0 Å in Y(tcpa)(Htcpa)$(H_2O)_5$ **(5.)**.

Atom1	Atom2	Symmetry code of Atom2	Distance (Å)
O9	O7	0.5-x, y, 0.5+z	2.6714
	O8	1-x, 1-y, 0.5+z	2.8148
	O10	x, y, z	2.8646
	O5	x, y, z	2.9095
	O1	x, y, z	2.9241
	O13	x, y, z	2.9394
O2	O1	x, y, z	2.1952
	O4	0.5-x, y, -0.5+z	2.5443
	O12	x, y, z	2.8920
	O11	x, y, z	2.9278
O11	O12	x, y, z	2.6741
	O6	-0.5+x, 1-y, z	2.7519
	O5	x, y, z	2.8799
	O2	x, y, z	2.9278
	O10	x, y, z	2.9554
O1	O2	x, y, z	2.1952
	O13	x, y, z	2.7725
	O9	x, y, z	2.9241
O8	O7	x, y, z	2.2255
	O10	0.5-x, y, -0.5+z	2.6318
	O13	1-x, 1-y, -0.5+z	2.7357
	O9	1-x, 1-y, -0.5+z	2.8148
O3	O4	x, y, z	2.2368
	O12	0.5-x, y, 0.5+z	2.7227

O13	O8	1-x, 1-y, 0.5+z	2.7357
	O1	x, y, z	2.7725
	O12	x, y, z	2.7825
	O5	0.5+x, 1-y, z	2.8503
	O9	x, y, z	2.9394
	O6	x, y, z	2.9946
O12	O7	0.5+x, 1-y, z	2.6514
	O11	x, y, z	2.6741
	O3	0.5-x, y, -0.5+z	2.7227
	O13	x, y, z	2.7825
	O2	x, y, z	2.8920
O7	O8	x, y, z	2.2255
	O12	-0.5+x, 1-y, z	2.6514
	O9	0.5-x, y, -0.5+z	2.6714
O10	O8	0.5-x, y, 0.5+z	2.6318
	O9	x, y, z	2.8646
	O5	x, y, z	2.9035
	O11	x, y, z	2.9554
O6	O5	x, y, z	2.1961
	O11	0.5+x, 1-y, z	2.7519
	O13	x, y, z	2.9946
O4	O3	x, y, z	2.2368
	O2	0.5-x, y, 0.5+z	2.5443
O5	O6	x, y, z	2.1961
	O13	-0.5+x, 1-y, z	2.8503
	O11	x, y, z	2.8799
	O10	x, y, z	2.9035
	O9	x, y, z	2.9095

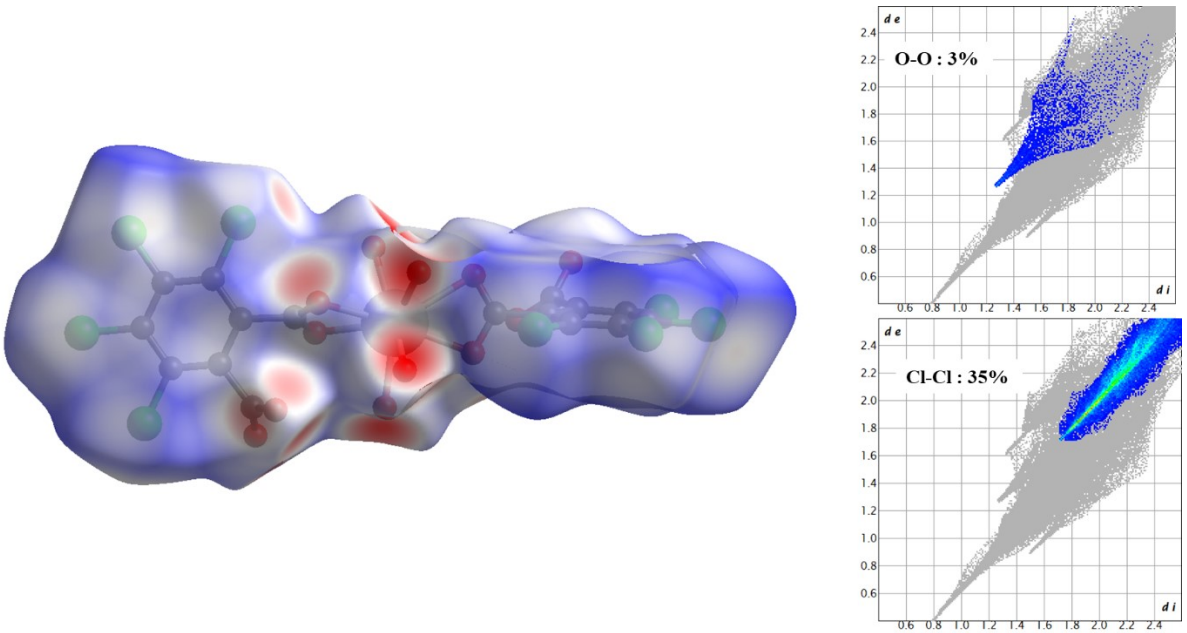

Figure S9. d_{norm} surface (left) and fingerprint plots (right) of the molecular motif of Y(tcpa)(Htcpa)$(H_2O)_5$ **(5.)**.

Table S16. Continuous Shape Measurements (CShM) for $[KTb(tcpa)_2(H_2O)_6 \cdot H_2O]_\infty$ **(6.)**. The lower is the CShM value, the better is the agreement with the given coordination polyhedron.

$[ML_8]$	OP-8	HPY-8	HBPY-8	CU-8	**SAPR-8**	TDD-8	JGBF-8	JETBPY-8	JBTPR-8	BTPR-8	JSD-8	TT-8	ETBPY-8
Tb	31.067	21.793	16.363	10.866	**1.282**	2.226	15.066	25.603	2.477	1.868	5.066	11.608	22.369

OP-8 ≡ D_{8h}-Octagon; HPY-8 ≡ C_{7v}-Heptagonal pyramid; HBPY-8 ≡ D_{6h}-Hexagonal bipyramid; CU-8 ≡ O_h-Cube; **SAPR-8 ≡ D_{4d}-Square antiprism**; TDD-8 ≡ D_{2d}-Triangular dodecahedron; JGBF-8 ≡ D_{2d}-Johnson gyrobifastigium J26; JETBPY-8 ≡ D_{3h}-Johnson elongated triangular bipyramid J14; JBTPR-8 ≡ C_{2v}-Biaugmented trigonal prism J50; BTPR-8 ≡ C_{2v}-Biaugmented trigonal prism; JSD-8 ≡ D_{2d}-Snub diphenoid J84; TT-8 ≡ T_d-Triakis tetrahedron; ETBPY-8 ≡ D_{3h}-Elongated trigonal bipyramid.

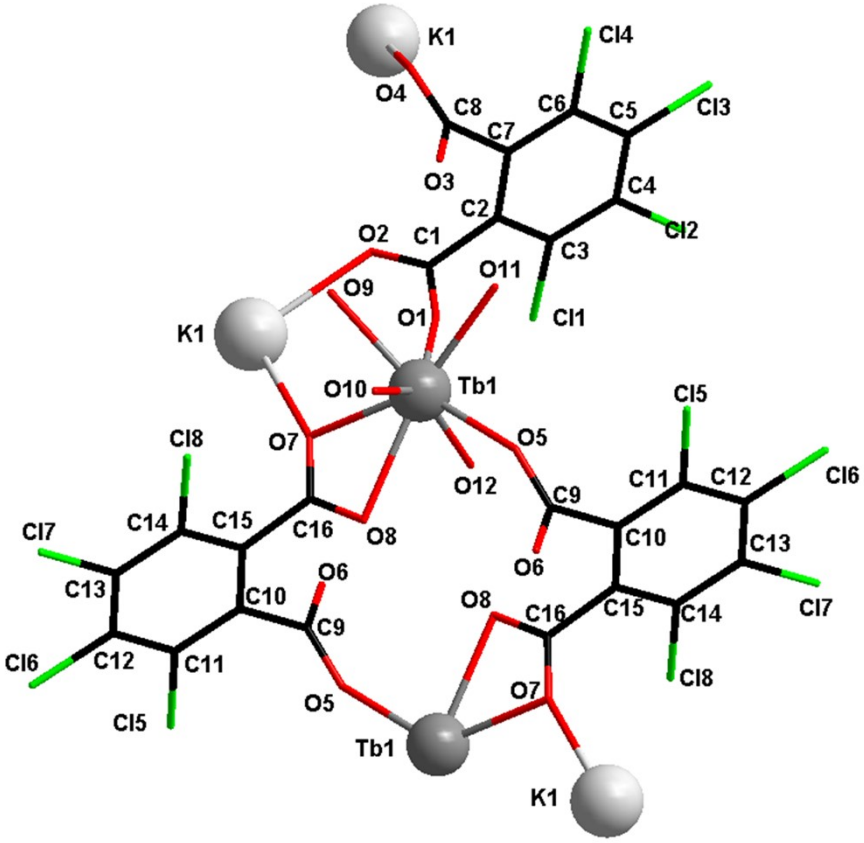

Figure S10. Extended asymmetric unit of $[KTb(tcpa)_2(H_2O)_6{\cdot}H_2O]_\infty$ **(6.)** with the numbering scheme. Hydrogen atoms have been omitted for clarity. K is in light grey and Tb in dark grey

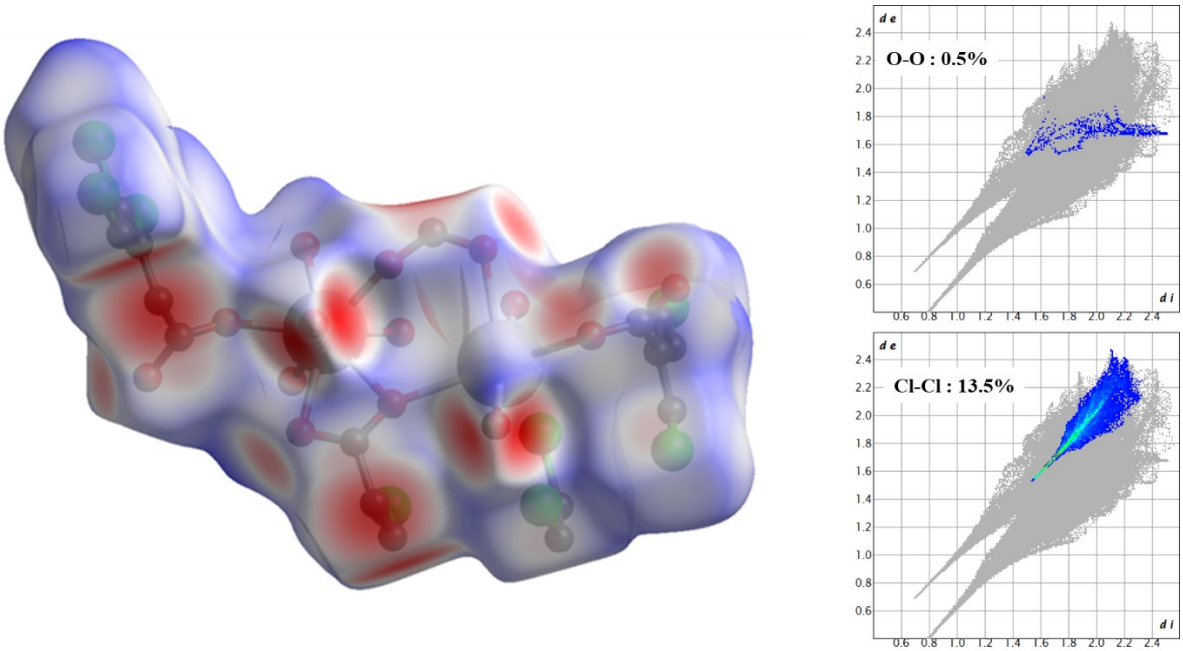

Figure S11. d_{norm} surface (left) and fingerprint plots (right) of the molecular motif of $[KTb(tcpa)_2(H_2O)_6{\cdot}H_2O]_\infty$ **(6.)**.

Table S17. O-O distances shorter than 3.0 Å in $[KTb(tcpa)_2(H_2O)_6 \cdot H_2O]_\infty$ **(6.)**.

Atom1	Atom2	Symmetry code of Atom2	Distance (Å)
O1	O2	x, y, z	2.2131
	O12	x, y, z	2.7279
	O9	x, y, z	2.8513
	O11	x, y, z	2.8526
O2	O1	x, y, z	2.2131
	O15	2-x, 2-y, 2-z	2.7064
O3	O4	x, y, z	2.2305
	O11	x, y, z	2.6741
	O9	1-x, 2-y, 2-z	2.7167
O4	O3	x, y, z	2.2305
	O10	1-x, 2-y, 2-z	2.7194
O5	O6	x, y, z	2.2255
	O11	x, y, z	2.9401
	O12	x, y, z	2.9543
	O10	x, y, z	2.9615
O6	O5	x, y, z	2.2255
	O13	-1+x, y, z	2.8243
	O14	1-x, 2-y, 1-z	2.8259
O7	O8	x, y, z	2.1993
	O9	1-x, 2-y, 1-z	2.9360
O8	O7	x, y, z	2.1993
	O12	x, y, z	2.7768
	O12	1-x, 2-y, 1-z	2.9101
O9	O3	1-x, 2-y, 2-z	2.7167
	O15	x, y, z	2.7225
	O10	x, y, z	2.7538
	O1	x, y, z	2.8513
	O7	1-x, 2-y, 1-z	2.9360
	O11	x, y, z	2.9780
O10	O4	1-x, 2-y, 2-z	2.7194
	O9	x, y, z	2.7538
	O13	-1+x, y, z	2.8665
	O5	x, y, z	2.9615
O11	O3	x, y, z	2.6741
	O1	x, y, z	2.8526
	O5	x, y, z	2.9401
	O9	x, y, z	2.9780
O12	O1	x, y, z	2.7279
	O8	x, y, z	2.7768
	O8	1-x, 2-y, 1-z	2.9101
	O13	x, y, z	2.9309
	O5	x, y, z	2.9543
O13	O6	1+x, y, z	2.8243
	O10	1+x, y, z	2.8665
	O12	x, y, z	2.9309
O14	O6	1-x, 2-y, 1-z	2.8259

O15	O2	2-x, 2-y, 2-z	2.7064
	O9	x, y, z	2.7225

Table S18. Cl-Cl distances shorter than 3.5 Å in $[KTb(tcpa)_2(H_2O)_6 \cdot H_2O]_\infty$ **(6.)**.

Atom1	Atom2	Symmetry code of Atom2	Distance (Å)
Cl1	Cl2	x, y, z	3.1281
	Cl5	1+x, y, z	3.4106
Cl2	Cl3	x, y, z	3.1178
	Cl1	x, y, z	3.1281
	Cl5	1+x, y, z	3.3346
Cl3	Cl4	x, y, z	3.1085
	Cl2	x, y, z	3.1178
Cl4	Cl3	x, y, z	3.1085
	Cl8	x, y, 1+z	3.2312
Cl5	Cl6	x, y, z	3.1130
	Cl2	-1+x, y, z	3.3346
	Cl1	-1+x, y, z	3.4106
Cl6	Cl5	x, y, z	3.1130
	Cl7	x, y, z	3.1138
Cl7	Cl6	x, y, z	3.1138
	Cl8	x, y, z	3.1246
Cl8	Cl7	x, y, z	3.1246
	Cl4	x, y, -1+z	3.2312