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ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

to

Tetranuclear oxido-bridged thorium(IV) clusters from the use of tridentate Schiff bases†‡

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† Dedicated to Professor Annie K. Powell on the occasion of her 60th birthday: A great scientist, an excellent mentor for the Patras group, a fantastic personality and a precious friend.

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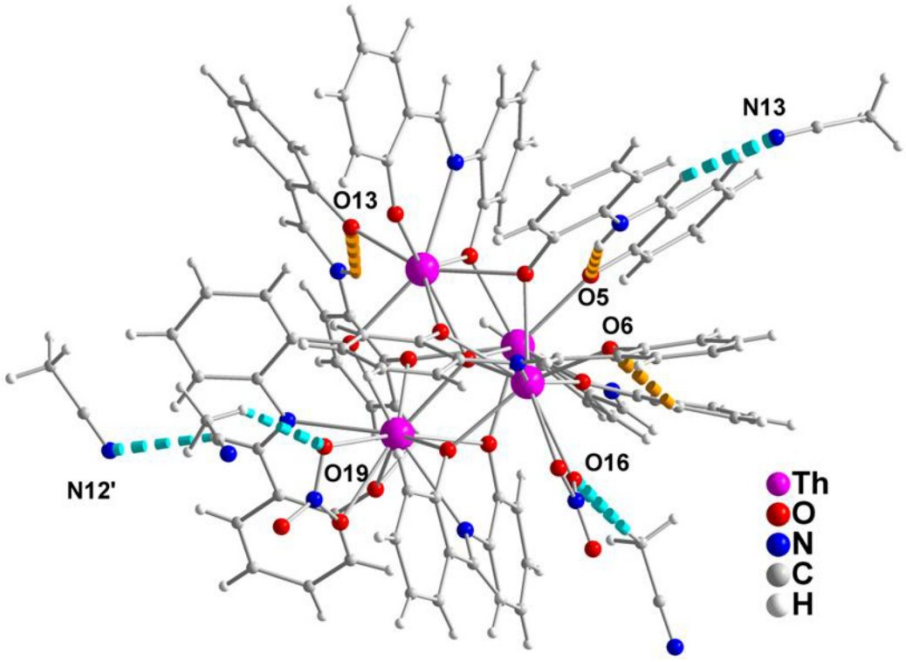

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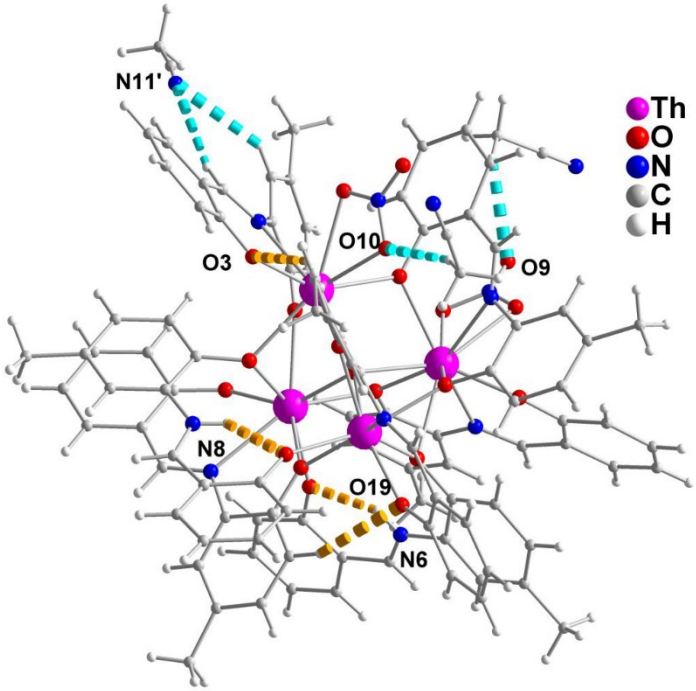

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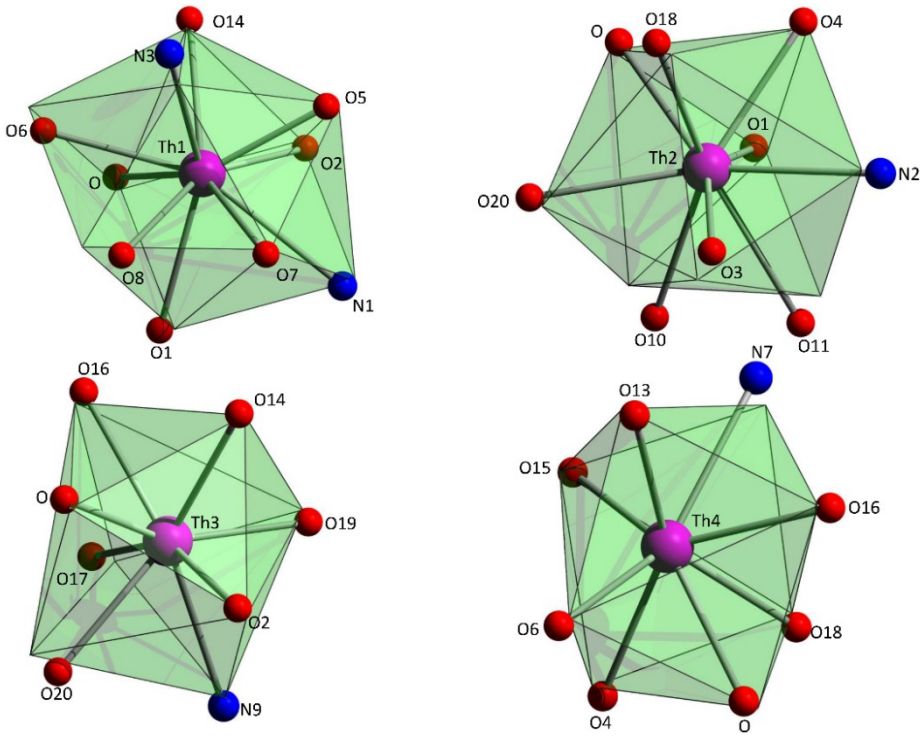

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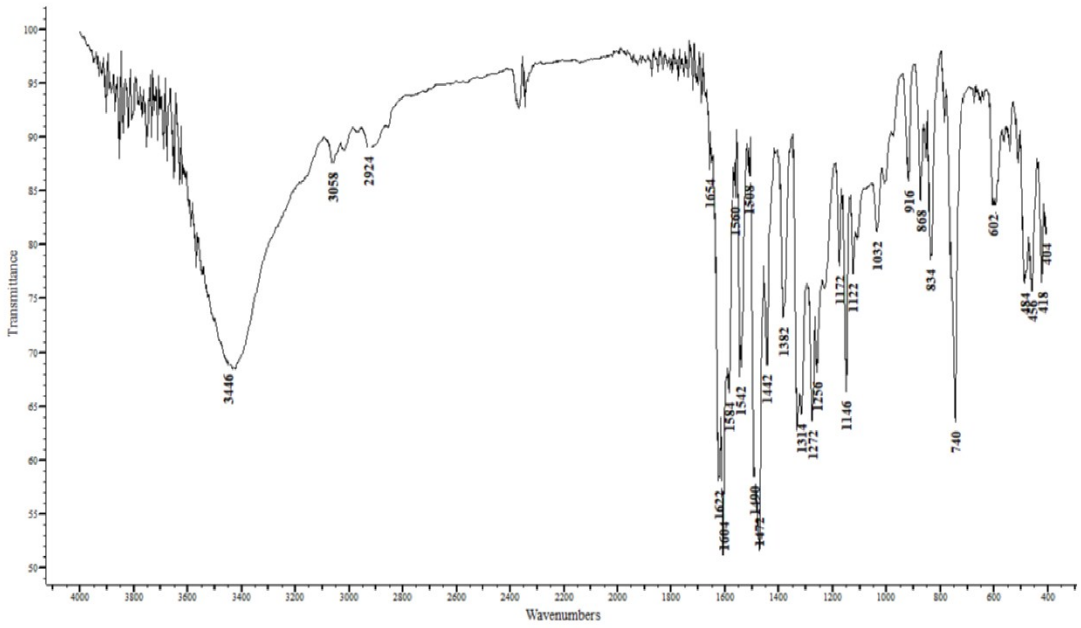

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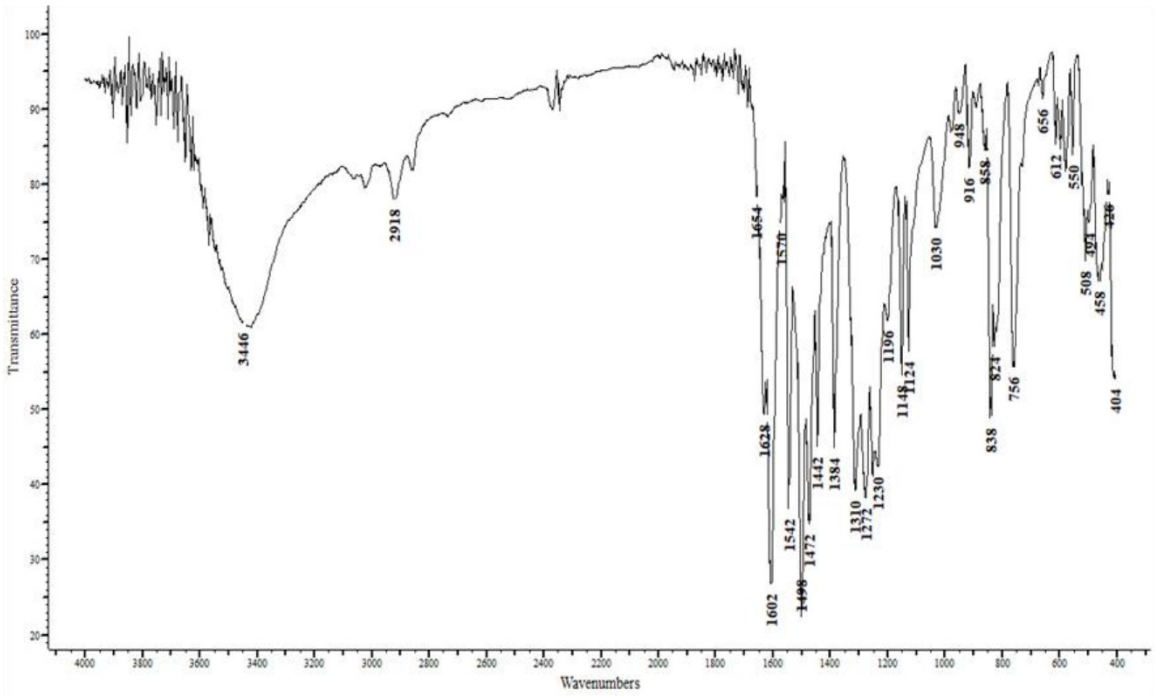

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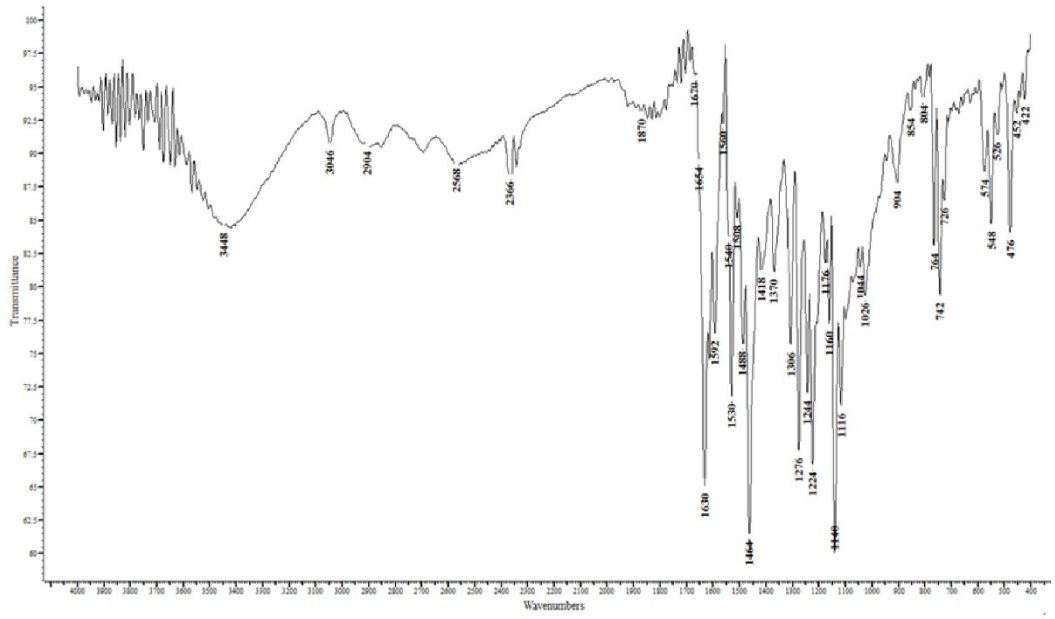

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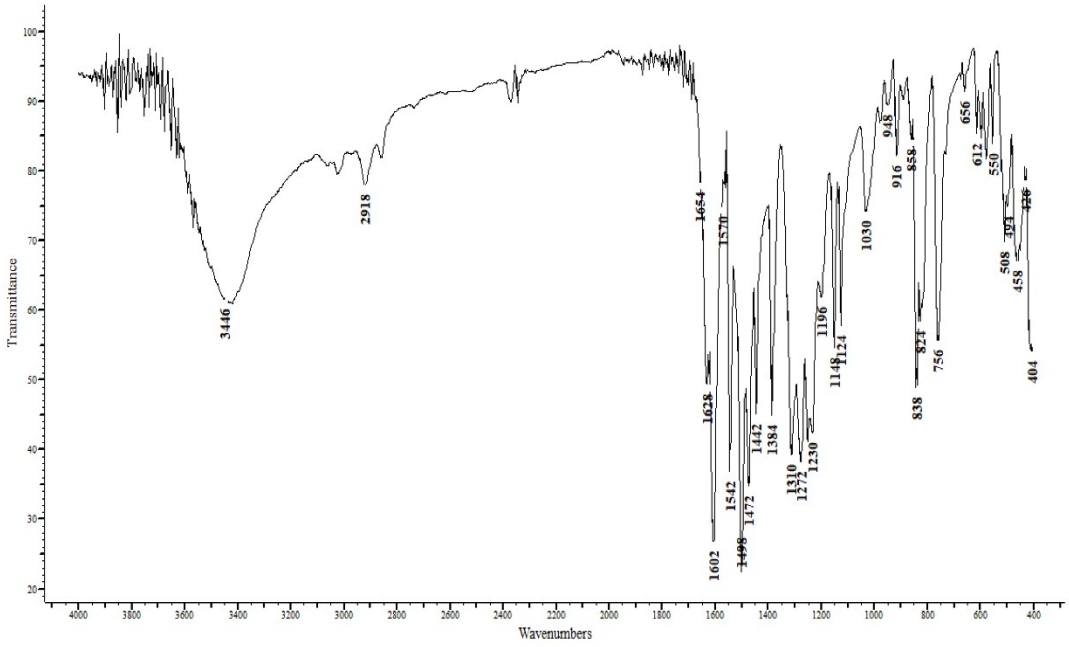

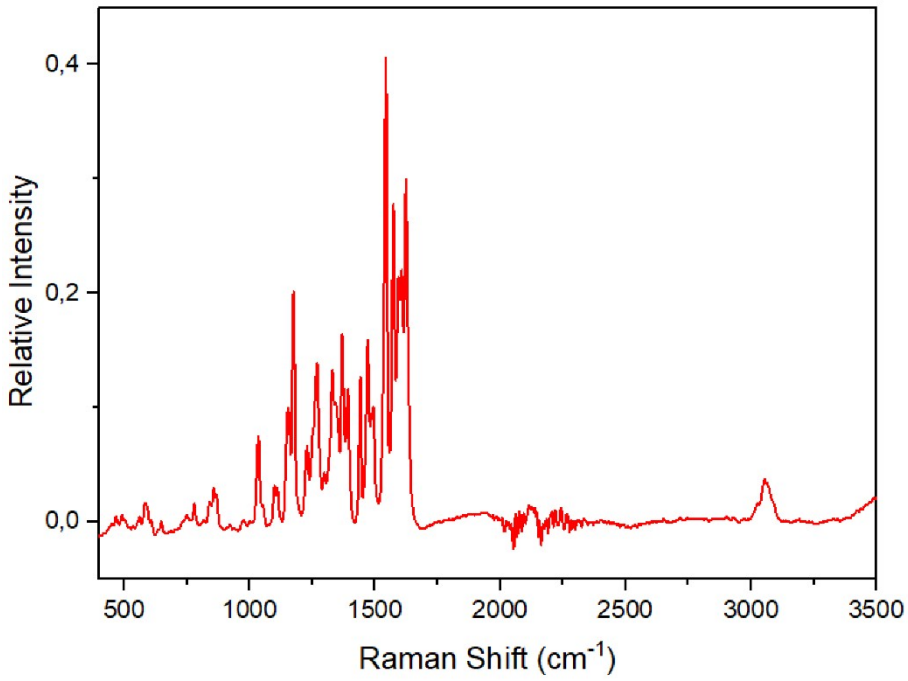

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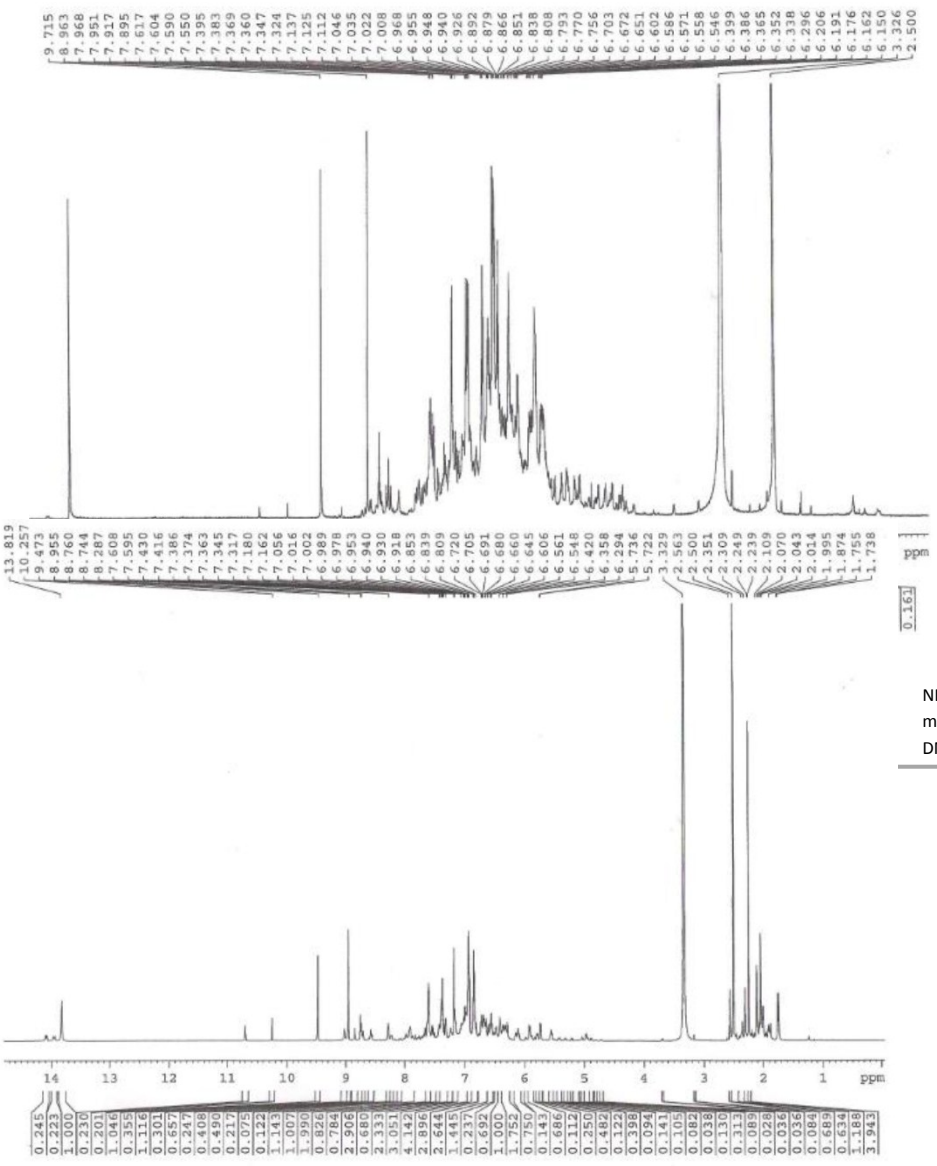

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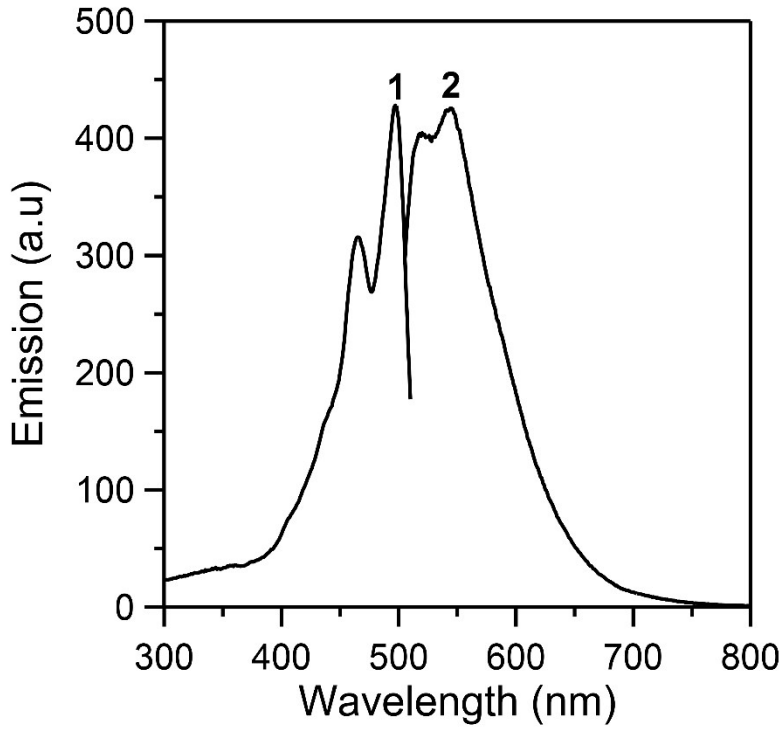

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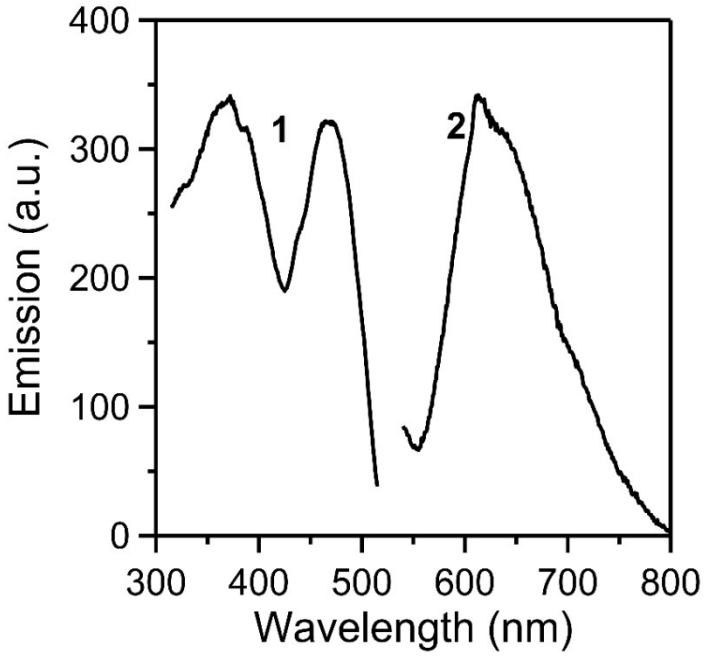

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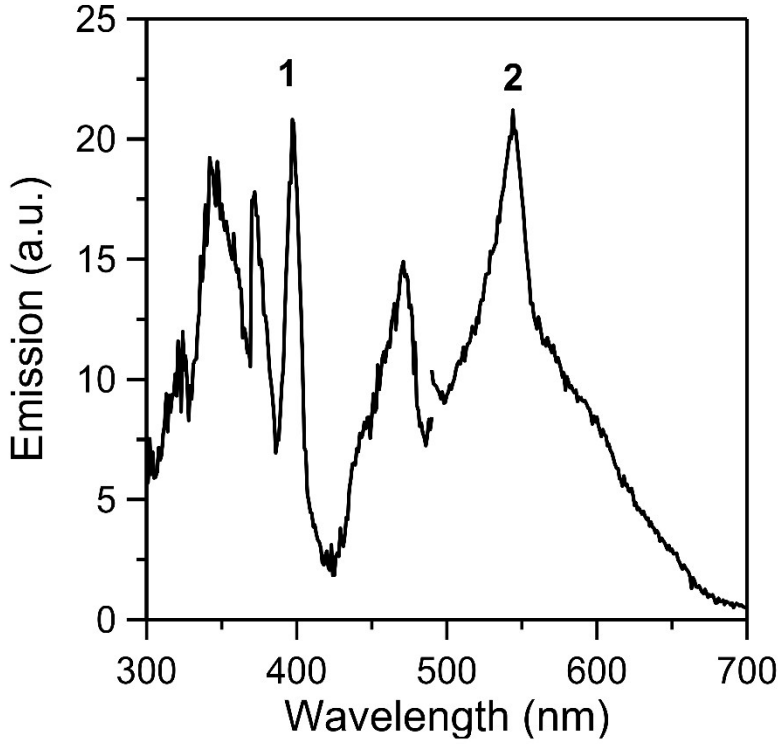

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Table S1 Metric parameters for the H bonds in the crystal structure of **1**·4MeCN[a, b]

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)	Symmetry of A
		INTRAMOLECULAR H BONDS			
N2-H(N2)···O5	0.82(5)	1.97(5)	2.649(5)	140(5)	*x*, *y*, *z*
N6-H(N6)···O13	0.88	2.01	2.685(5)	133	*x*, *y*, *z*
C41-H(C41)···O6	1.00(6)	2.33(6)	3.127(6)	136(4)	*x*, *y*, *z*
		INTERMOLECULAR H BONDS			
C20-H(C20)···N13	0.92(5)	2.54(5)	3.411(8)	158(4)	*x*, *y*, *z*
C85-H(C85)···N12	1.06(4)	2.69(4)	3.662(9)	153(3)	-*x*+1, -*y*+1, -*z*
C93-H_B(C93)···O16	0.98	2.39	3.339(8)	164	*x*, *y*, *z*
C95-H_A(C95)···O19	0.98	2.52	3.369(8)	144	*x*, *y*, *z*
C99-H_C(C99)···N10	0.98	2.46	3.407(12)	163	*x*-1, *y*, *z*
C5-H(C5)···O20[c]	0.92(5)	2.47(5)	3.160(6)	132(4)	*x*-1, *y*, *z*
C7-H(C7)···O21[c]	0.96(5)	2.58(5)	3.501(6)	160(4)	*x*-1, *y*, *z*

[a] Atoms C93, C95, C97 and C99 belong to the lattice MeCN molecules; the corresponding nitrogen atoms are N10, N11, N12 and N13.
[b] A= acceptor, D=donor.
[c] These H-bonding interactions link directly the tetranuclear cluster molecules.

Table S2 Metric parameters for the H bonds in the crystal structure of **2**·2.4MeCN[a,b,c]

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)	Symmetry of A
		INTRAMOLECULAR H BONDS			
N6-H(N6)···O13	0.88	1.97	2.663(5)	134	*x*, *y*, *z*
N8-H(N8)···O17	0.88	1.96	2.655(5)	135	*x*, *y*, *z*
C69-H(C69)···O19	0.95	2.64	3.528(6)	156	*x*, *y*, *z*
C97-H(C97)···O3	0.95	2.42	3.169(6)	136	*x*, *y*, *z*
		INTERMOLECULAR H BONDS			
C100-H_B(C100)···O10	0.98	2.58	3.500(8)	156	*x*, *y*, *z*
C21-H(C21)···N11	0.95	2.65	3.568(11)	163	*x*-1, *y*, *z*
C23-H(C23)···N11	0.95	2.62	3.443(10)	145	*x*-1, *y*, *z*
C104-H_I(C104)···O9	0.98	2.65	3.368(11)	130	*x*, *y*, *z*
C49-H(C49)···O12[c]	0.95	2.17	3.057(6)	153	-*x*+1/2, *y*+1/2, -*z*+3/2
C79-H(C79)···O9[c]	0.95	2.62	3.473(6)	150	*x*-1/2, -*y*+1/2, *z*-1/2

[a] Atoms C100, C104, N10, N11 and N12 belong to lattice MeCN.

[b] A= acceptor, D=donor.

[c] These H-bonding interactions link directly the tetranuclear cluster molecules.

Table S3 Continuous Shape Measures (CShM) values for the potential coordination polyhedra of the 8-coordinate Th^{IV} centres in the structures of complexes $[Th_4O(NO_3)_2(LH)_2(L)_5]\cdot 4MeCN$ (**1**·4MeCN) and $[Th_4O(NO_3)_2(L'H)_2(L')_5]\cdot 2.4MeCN$ (**2**·2.4MeCN)[a]

Ideal coordination polyhedron	Compound **1**·4MeCN		Compound **2**·2.4MeCN	
	Th1	Th3	Th3	Th4
Octagon (OP-8)	31.505	30.457	30.360	30.735
Heptagonal pyramid (HPY-8)	23.306	23.129	22.648	22.875
Hexagonal bipyramid (HBPY-8)	15.159	15.220	15.183	14.460
Cube (CU-8)	9.797	11.058	10.887	10.021
Square antiprism (SARP-8)	2.752	2.803	2.694	2.665
Triangular dodecahedron (TDD-8)	**1.334**	2.387	1.987	**1.893**
Johnson gyrobifastigium (JGBF-8)	13.045	11.604	11.650	12.051
Johnson elongated triangular bipyramid (JETBPY-8)	24.615	24.263	24.805	23.766
Biaugmented trigonal prism J50 (JBTPR-8)	2.324	**1.734**	**1.710**	2.420
Biaugmented trigonal prism (BTPR-8)	2.432	1.985	1.890	2.445
Snub diphenoid J84 (JSD-8)	3.304	3.682	3.705	4.014
Triakis tetrahedron (TT-8)	10.538	11.806	11.546	10.847
Elongated trigonal bipyramid (ETBPY-8)	20.072	21.261	21.034	18.935

[a] The polyhedron with the CShM value in bold is the real coordination polyhedron of the corresponding Th^{IV} centre for each compound.

Table S4 Continuous Shape Measures (CShM) values for the potential coordination polyhedra of the 9-coordinate Th^{IV} centres in the structures of complexes $[Th_4O(NO_3)_2(LH)_2(L)_5]\cdot 4MeCN$ (**1**·4MeCN) and $[Th_4O(NO_3)_2(L'H)_2(L')_5]\cdot 2.4MeCN$ (**2**·2.4MeCN)[a]

Ideal coordination polyhedron	Compound **1**·4MeCN	Compound **2**·2.4MeCN
	Th2	Th2
Enneagon (EP-9)	33.865	33.290
Octagonal pyramid (OPY-9)	21.503	20.990
Heptagonal bipyramid (HBPY-9)	11.318	11.879
Johnson triangular cupola (JTC-9)	13.863	13.923
Capped cube J8 (JCCU-9)	9.476	9.539
Spherical-relaxed capped cube (CCU-9)	7.831	7.884
Capped square antiprism J10 (JCSAPR-9)	5.330	4.913
Spherical capped square antiprism (CSAPR-9)	4.278	3.932
Tricapped trigonal prism J51 (JTCTPR-9)	5.675	5.417
Spherical tricapped trigonal prism (TCTPR-9)	5.099	4.860
Tridiminished icosahedron J63 (JTDIC-9)	12.795	12.556
Hula-hoop (HH-9)	6.853	6.679
Muffin (MFF-9)	**3.067**	**2.836**

[a] The polyhedron with the CShM value in bold is the real coordination polyhedron of the corresponding Th^{IV} centre for each compound.

Table S5 Continuous Shape Measures (CShM) values for the potential coordination polyhedra of the 10-coordinate Th^{IV} centres in the structures of complexes $[Th_4O(NO_3)_2(LH)_2(L)_5]\cdot 4MeCN$ (**1**·4MeCN) and $[Th_4O(NO_3)_2(L'H)_2(L')_5]\cdot 2.4MeCN$ (**2**·2.4MeCN)[a]

Ideal coordination polyhedron	Compound **1**·4MeCN	Compound **2**·2.4MeCN
	Th4	Th1
Decagon (DP-10)	34.132	31.410
Enneagonal pyramid (EPY-10)	21.502	22.444
Octagonal bipyramid (OBPY-10)	17.520	18.160
Pentagonal prism (PPR-10)	10.412	9.427
Pentagonal antiprism (PAPR-10)	12.861	12.457
Bicapped cube J15 (JBCCU-10)	12.620	12.929
Bicapped square antiprism J17 (JBCSAPR-10)	4.655	4.916
Metabidiminished icosahedron J62 (JMBIC-10)	8.964	8.866
Augmented tridiminished icosahedron J64 (JATDI-10)	17.842	18.342
Sphenocorona J87 (JSPC-10)	**1.834**	**2.309**
Staggered dodecahedron (2:6:2) [SDD-10]	4.968	5.204
Tetradecahedron (2:6:2) [TD-10]	4.037	4.718
Hexadecahedron (2:6:2) or (1:4:4:1) [HD-10]	10.136	10.294

[a] The polyhedron with the CShM value in bold is the real coordination polyhedron of the corresponding Th^{IV} centre for each compound.