Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary informations

Bottom-up synthesis of functionalized {$Ce_4(SiW_9O_{34})_2(L)_2$} polyoxometalates

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Table S1: Crystal data and structure refinement for compounds **1-5**.

	(1)	**(2)**	**(3)**	**(4)**	**(5)**
Formula	$C_8H_{10}Ce_4Na_{10}O_{106}Si_2W_{18}$	$C_{10}H_{13}Ce_4Cs_{2.5}Na_{7.5}O_{101}Si_2W_{18}$	$C_{10}H_{22}Ce_4N_2K_4Na_4O_{98}Si_2W_{18}$	$C_{12}H_{42}Ce_4N_6Na_4O_{94.7}Si_2W_{18}$	$Ce_9Cs_{3.25}Na_7O_{182.25}Si_4W_{36}$
Formula weight	5958.02	6179.86	5912.62	5803.64	11500.93
Temperature/K	100	100	296.15	100	100
Crystal color	Yellow	yellow	yellow	yellow	Yellow
Crystal size/mm	0.08 x 0.02 x 0.01	0.10 x 0.05 x 0.05	0.06 x 0.06 x 0.01	0.16 x 0.13 x 0.11	0.20 x 0.12 x 0.05
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	*P*-1	*P*-1	*P*-1
a/Å	13.5499(3)	13.2090(7)	12.8048(9)	12.7662(4)	18.7410(11)
b/Å	12.9776(3)	12.8421(6)	13.6116(9)	13.7583(5)	21.5447(12)
c/Å	26.9266(6)	28.4056(14)	15.3227(11)	15.2105(6)	30.6060(16)
α/°	90	90	79.826(2)	79.2760(19)	70.021(3)
β/°	98.2429(13)	98.754(3)	74.283(2)	75.0343(17)	86.051(3)
γ°	90	90	65.695(2)	65.2698(15)	66.330(3)
Volume/$Å^3$	4686.00(18)	4762.3(4)	2336.5(3)	2334.98(15)	10603.5(11)
Z, $\rho_{calculated}$/g.cm^{-3}	4, 4.223	4, 4.310	2, 4.202	2, 4.127	2, 3.602
μ/mm^{-1}	24.094	24.633	24.303	24.139	22.005
Θ range/°	1.528 – 36.28	1.451 – 26.492	2.49 – 26.36	1.636 – 30.526	0.71 – 26.403
Limiting indices	$-22 \le h \le 22$ $-21 \le k \le 21$ $-44 \le l \le 44$	$-16 \le h \le 16$ $-16 \le k \le 16$ $-35 \le l \le 35$	$-15 \le h \le 15$ $-16 \le k \le 16$ $-19 \le l \le 18$	$-18 \le h \le 17$ $-19 \le k \le 19$ $-21 \le l \le 21$	$-23 \le h \le 23$ $-26 \le k \le 26$ $-38 \le l \le 38$
Collected reflections	223683	106571	41566	87632	308589
Unique reflections	22562 [R(int) = 0.0550]	9773 [R(int) = 0.0495]	9482 [R(int) = 0.0446]	14135 [R(int) = 0.0470]	43321 [R(int) = 0.0768]
Parameters	711	413	644	686	1513
Goodness-of-fit on F^2	1.052	1.104	1.035	1.019	1.080
Final R indices [$I>2\sigma(I)$]	R1 = 0.0291 wR2 = 0.0532	R1 = 0.0637 wR2 = 0.1934	R1 =0.0288 wR2 = 0.0828	R1 = 0.0262 wR2 = 0.0586	R1 =0.0658 wR2 = 0.1510
R indices (all data)	R1 = 0.0411 wR2 = 0.0561	R1 = 0.0653 wR2 = 0.1963	R1 =0.0342 wR2 =0.0859	R1 = 0.0337 wR2 = 0.0612	R1 =0.1097 wR2 =0.1873
Largest diff. peak and hole/e.Å^{-3}	2.93 and -2.95	3.70 and -3.39	1.85 and -2.19	3.77 and -2.12	6.08 and -4.21

Table S2: Comparison of $\{SiW_9O_{34}\}$ main vibrations (cm^{-1}) of compounds **1 - 5**.

	W-Od	W-Ob-W	W-Oc-W
Compound **1**	996	949	873, 769, 713 and 637
Compound **2**	994	950	873, 773, 714 and 674
Compound **3**	1000 and 989(sh)	948	873, 793, 698 and 649
Compound **4**	1003 and 988(sh)	946	873, 793, 716 and 674
Compound **5**	1011 and 989(sh)	938	861, 723 and 664
SiW_9O_{34}	984	919	885, 802 and 682

Table S3: Comparison of bond distances (Å) for compounds **1-2**.

	Compound **1**		Compound **2**	
	Ce_{int}	Ce_{ext}	Ce_{int}	Ce_{ext}
M-(O_{POMax})	2.546(3)-2.564(3)	2.267(4)-2.415(3)	2.571(18)-2.583(18)	2.271(18)-2.414(20)
M-(O_{POMeq})	2.248(4)-2.403(3)	2.497(4)-2.498(3)	2.246(19)-2.420(17)	2.495(17)-2.499(19)
M-(μ^3-O)	2.228(3)-2.230(4)	2.126(3)	2.223(17)-2.233(17)	2.132(16)
M-(O_L)		2.432(4)-2.480(3)		2.399(15)-2.448(20)

Table S4: Comparison of bond distances (Å) for compounds **3-4**.

	Compound **3**		Compound **4**	
	Ce_{int}	Ce_{ext}	Ce_{int}	Ce_{ext}
M-(O_{POMax})	2.566(6)-2.608(6)	2.251(5)-2.432(5)	2.560(4)-2.605(4)	2.254(4)-2.410(4)
M-(O_{POMeq})	2.222(5)-2.429(7)	2.488(5)-2.505(7)	2.235(4)-2.418(5)	2.476(4)-2.495(3)
M-(μ^3-O)	2.208(6)-2.228(4)	2.146(6)	2.216(5)-2.233(3)	2.138(5)
M-(O_L)		2.427(6)-2.471(8)		2.440(4)-2.476(6)

Table S5: BVS calculations for compounds **1-5**.

BVS for compound **1**			Attribution
	Ce^{III}	Ce^{IV}	
Ce_{int}	4.34	3.83	Ce^{4+}
Ce_{ext}	4.17	3.67	Ce^{4+}
μ^3-O	2.42	2.13	O^{2-}

BVS for compound **2**			Attribution
	Ce^{III}	Ce^{IV}	
Ce_{int}	4.43	3.89	Ce^{4+}
Ce_{ext}	4.19	3.69	Ce^{4+}
μ^3-O	2.39	2.10	O^{2-}

BVS for compound **3**			Attribution
	Ce^{III}	Ce^{IV}	
Ce_{int}	4.30	3.79	Ce^{4+}
Ce_{ext}	4.23	3.72	Ce^{4+}
μ^3-O	2.41	2.13	O^{2-}

BVS for compound **4**			Attribution
	Ce^{III}	Ce^{IV}	
Ce_{int}	4.32	3.80	Ce^{4+}
Ce_{ext}	4.30	3.69	Ce^{4+}
μ^3-O	2.41	2.12	O^{2-}

BVS for compound **5**			Attribution
	Ce^{III}	Ce^{IV}	
Ce_1	3.63	3.83	Ce^{4+}
Ce_2	3.71	3.91	Ce^{4+}
Ce_3	3.46	3.88	Ce^{4+}
Ce_4	4.41	3.88	Ce^{4+}
Ce_5	4.34	3.82	Ce^{4+}
Ce_6	4.28	3.77	Ce^{4+}
Ce_7	4.28	3.77	Ce^{4+}
Ce_8	4.36	3.84	Ce^{4+}
Ce_9	4.06	3.58	Ce^{4+}
μ^3-O_{111}		1.96	O^{2-}
μ^2-O_{112}		1.37	OH^-
μ^2-O_{113}		0.65	OH^-/H_2O
μ^2-O_{114}		1.37	OH^-

Table S6: ^{183}W chemical shifts for compound (**1-4**).

Compound	δ (ppm) / relative intensity / $\Delta\nu_{1/2}$ (Hz)	
	Belt	Cap
$\{Ce_4(\mu^3\text{-}O)_2(SiW_9O_{34})_2(Succ)_2\}$ (**1**)	-170.9 / 2 / 5.2 -175.9 / 2 / 9.7(a) -179.7 / 2 / 5	-145.3 / 1 / 4.8 -175.9 / 2 / 9.7(a)
$\{Ce_4(\mu^3\text{-}O)_2(SiW_9O_{34})_2(Glu)_2\}$ (**2**)	-172.5 / 2 / 5 -178.6 / 2 / 10 -181.5 / 2 / 4	-145.2 / 1 / 5 -177.3 / 2 / 11
$\{Ce_4(\mu^3\text{-}O)_2(SiW_9O_{34})_2(NH_3^+\text{-val})_2\}$ (**3**)	-168.3 / 2 / 5.8 -177.2 / 2 / 5.8 -179.7 / 2 / 5.8	-145.4 / 1 / 5.3 -174.3 / 2 / 6.5
$\{Ce_4(\mu^3\text{-}O)_2(SiW_9O_{34})_2(NH_3^+\text{-Cap})_2\}$ (**4**)	-168 / 2 / 5.5 -177.1 / 2 / 5.9 -178.7 / 2 / 5.2	-147.5 / 1 / 4.6 -173.3 / 2 / 4.8

(a) This two signals appear to be overlapping thus generating a broader signal integrating for four tungsten atoms.

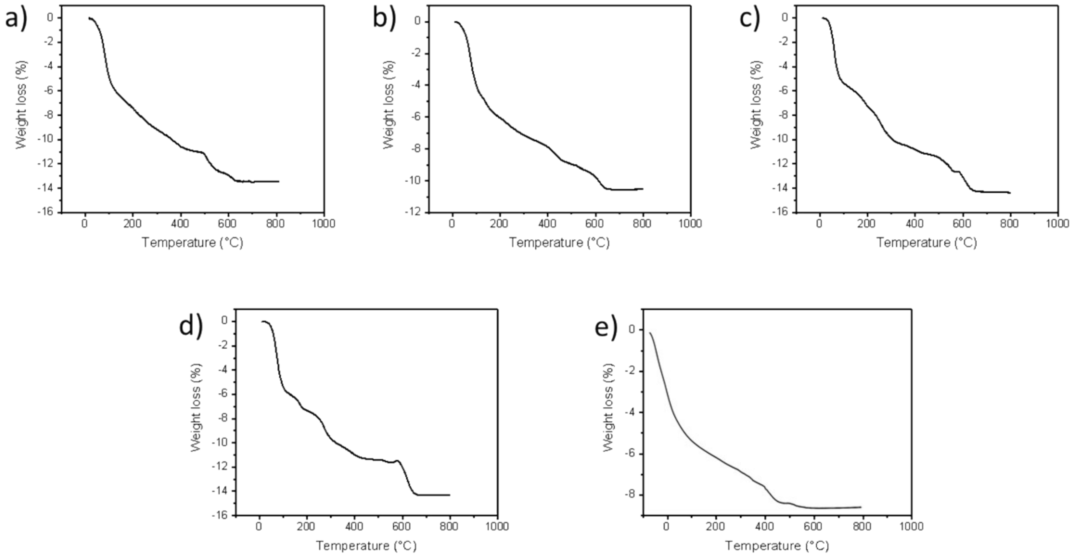

Figure S1: TGA of compound **1** (a), **2** (b), **3** (c), **4** (d) and **5** (e).

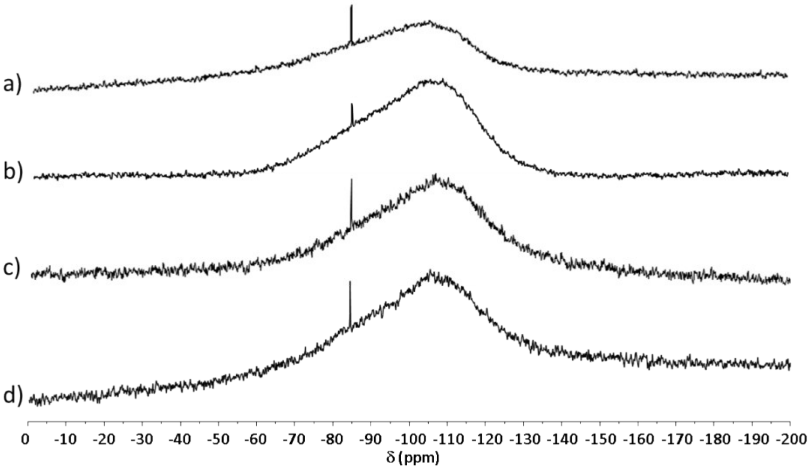

Figure S2. ^{29}Si NMR spectroscopy of compound 1 (a), compound 2 (b), compound 3 (c) and compound 4 (d) in a D_2O/H_2O solvent.

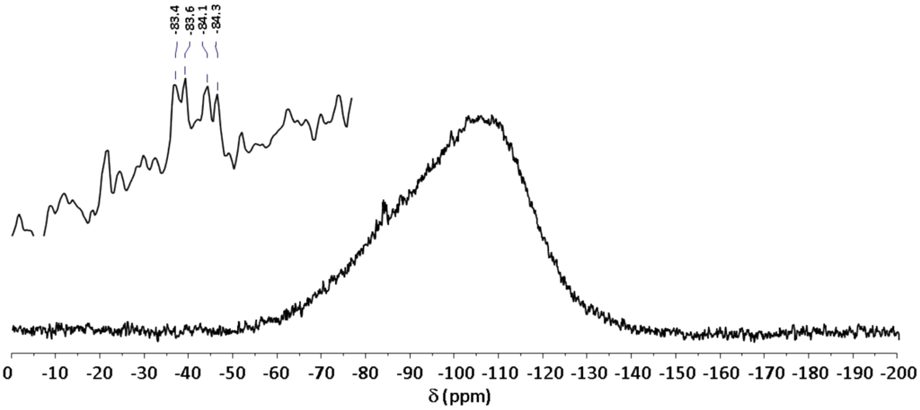

Figure S3. ^{29}Si NMR spectroscopy of compound 5 in a D_2O/H_2O solvent showing an insert around the four observed silicon signals.

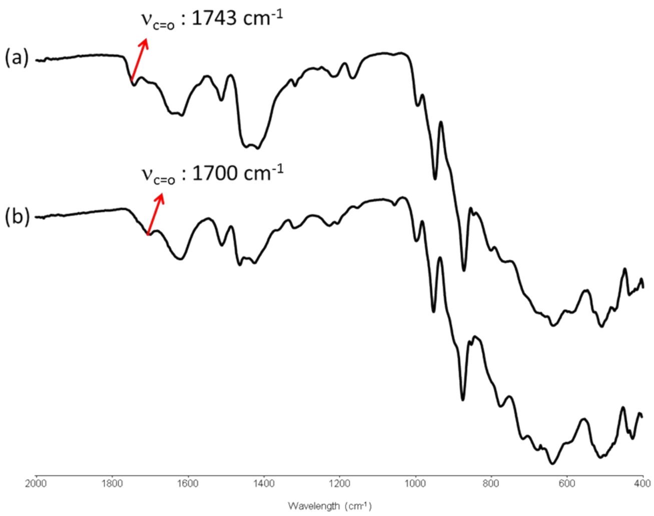

Figure S4. IR spectra of compound 1 (a) and compound 2 (b) highlighting the carbonyl vibration of the protonated free acid arm.

Special details on the refinement of compounds **1-3**:

Compound **1**:

Alert A:

```
Short Inter D...A Contact Ow14 .. Ow12
```

This alert is probably due to some disorder arising in the water molecule of the lattice as Ow12 was set to be at a 0.2 occupancy factor. This type of disorder is frequently encountered in polyanionic structures.

```
Check Calcd Positive Residual Density on Na1, Na4 and Na5
```

The absorption correction was applied on the basis of multiple measurements of equivalent reflections and was done using a semi empirical absorption correction. It is possible that these alerts are due to some inefficiency in the absorption correction.

Alert B:

```
Isolated Oxygen Atom (H-atoms Missing ?)/ D-H Without Acceptor O39 -- H39
```

This alert is due to the presence of the oxygen atoms of the water molecules present in the lattice of the crystals. Generally, in polyoxometalate structural resolution, hydrogen atoms are not added on calculated positions to these water-oxygen atoms because they do not reflect the disorder that can be present around them.

```
Non-Solvent Resd 1 O Ueq(max)/Ueq(min) Range 10 Ratio
```

This alert is due to the thermal mobility of one oxygen atom generating larger U(eq) value than generally observed.

```
Check Calcd Residual Density 0.19A From Ow11
```

This alert and the following ones probably occur here due to the presence of some disorder in the water molecules of the lattice that where not modeled due to close proximity with the already placed atoms.

Compound **2**:

Alert A:

```
Isotropic non-H Atoms in Anion/Solvent
```

Several oxygen and carbon atoms of the polyanionic part were not refined anisotropically because some of them appear to be NPD if refined anisotropically. Thus, for more reliability, we decided to refine them isotropically. Only the heaviest atoms were refined anisotropically in this compound.

```
Short Inter D...A Contact Ow11 .. Ow12
```

These alerts are probably due to some disorder arising in the water molecule of the lattice.

Alert B:

```
Isolated Oxygen Atom (H-atoms Missing ?)
```

This alert is due to the presence of the oxygen atoms of the water molecules present in the lattice of the crystals. Generally, in polyoxometalate structural resolution, hydrogen atoms are not added on calculated position to these water-oxygen atoms because they do not reflect the disorder that can be present around them.

```
Short Inter D...A Contact Ow5 .. Ow6
```

These alerts probably occur here due to the presence of some disorder in the water molecules of the lattice generating larger sphere/ellipsoids for the modeling of the water molecules.

```
Check Twin Law ( 0 0 1)[ 1 0 3] Estimated BASF 0.09
```

A twin law was found. It enables an enhancement of the correlation factors of the structural resolution from R1 = 11.78%, wR2 = 30.72% to R1 = 6.36%, wR2 = 19.63% with the twin law which seems in better agreement with the R_{int} = 4.92% of the data.

Compound **3**:

Alert B:

```
Atom O6 has ADP max/min Ratio / Non-Solvent Resd 1 O Ueq(max)/Ueq(min) Range
```

These alerts are generated by a really flat ellipsoid, nearly NPD of the O6 oxygen atoms.

```
High 'MainMol' Ueq as Compared to Neighbors of
```

This alert is due to a disordered water molecule in the lattice or one C atom of the organic part of the polyanionic moieties generating elongated ellipsoid anisotropy probably because they are disordered on two close positions.

`Isolated Oxygen Atom (H-atoms Missing ?)`

This alert is due to the presence of the oxygen atoms of the water molecules present in the lattice of the crystals. Generally, in polyoxometalate structural resolution, hydrogen atoms are not added on calculated position to these water-oxygen atoms because they do not reflect the disorder that can be present around them.

`Short Inter D...A Contact O1 ..O3W`

These alerts probably occur here due to the presence of some disorder in the water molecules of the lattice generating larger sphere/ellipsoids for the modeling of the water molecules.

`Check Calcd Residual Density 0.82A From`

This residual density may be due to a inaccurate modeling of the anisotropy of the neighboring W1 atom.

Compound **4**:

Alert A:

`Atom O6 has ADP max/min Ratio`

This alert is generated by a really flat ellipsoid, nearly NPD of the O6 oxygen atoms.

`Check Calcd Residual Density 1.35A From O4 and O6`

This alert is due to an α–β disorder has it was observed in compound 1. It was modelled but was not conserved as the disorder ratio (ca. 99/1 for α–β) was extremely weak.

Alert B:

`Non-Solvent Resd 1 O Ueq(max)/Ueq(min) Range`

This alert is due to the thermal mobility of one oxygen atom generating larger U(eq) value than generally observed.

`Isolated Oxygen Atom (H-atoms Missing ?)`

This alert is due to the presence of the oxygen atoms of the water molecules present in the lattice of the crystals. Hydrogen atoms are not added on calculated position to these water-oxygen atoms because they do not reflect the disorder that can be present around them.

`Short Inter D...A Contact O4 .. Ow4`

These alerts probably occur here due to the presence of some disorder in the water molecules of the lattice generating larger sphere/ellipsoids for the modeling of the water molecules.

`Check Calcd Residual Density 0.96A From O2`

This alert is due to an α–β disorder has it was observed in compound 1. It was modelled but was not conserved as the disorder ratio (ca. 99/1 for α–β) was extremely weak.

Compound **5**:

Alert A:

`Check Calcd Positive Resid. Density on W24`

The absorption correction was applied on the basis of multiple measurements of equivalent reflections and was done using a semi empirical absorption correction. It is possible that these alerts are due to some inefficiency in the absorption correction.

Alert B:

`Atom Si3 has ADP max/min Ratio`

This alert reflect the nearly NPD state of the silicon atom

`Non-Solvent Resd 1 O Ueq(max)/Ueq(min) Range`

`Large Hirshfeld Difference Ce8 --O113`

`High ’MainMol’ Ueq as Compared to Neighbors of`

These alerts are due to the thermal mobility of one oxygen atom (O113) in the polyanion moieties generating larger U(eq) value in comparison of the two neighboring tungsten atoms. As stated in the manuscript, this oxygen atom is thermally disordered. Its BVS is average between a water molecule and a hydroxo bridge generating this disorder.

`Isolated Oxygen Atom (H-atoms Missing ?)`

This alert is due to the presence of the oxygen atoms of the water molecules present in the lattice of the crystals. Hydrogen atoms are not added on calculated position to these water-oxygen atoms because they do not reflect the disorder that can be present around them.