Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary information for:

An {Fe_{60}} tetrahedral cage: building nanoscopic molecular assemblies through cyanometallate and alkoxo linkers

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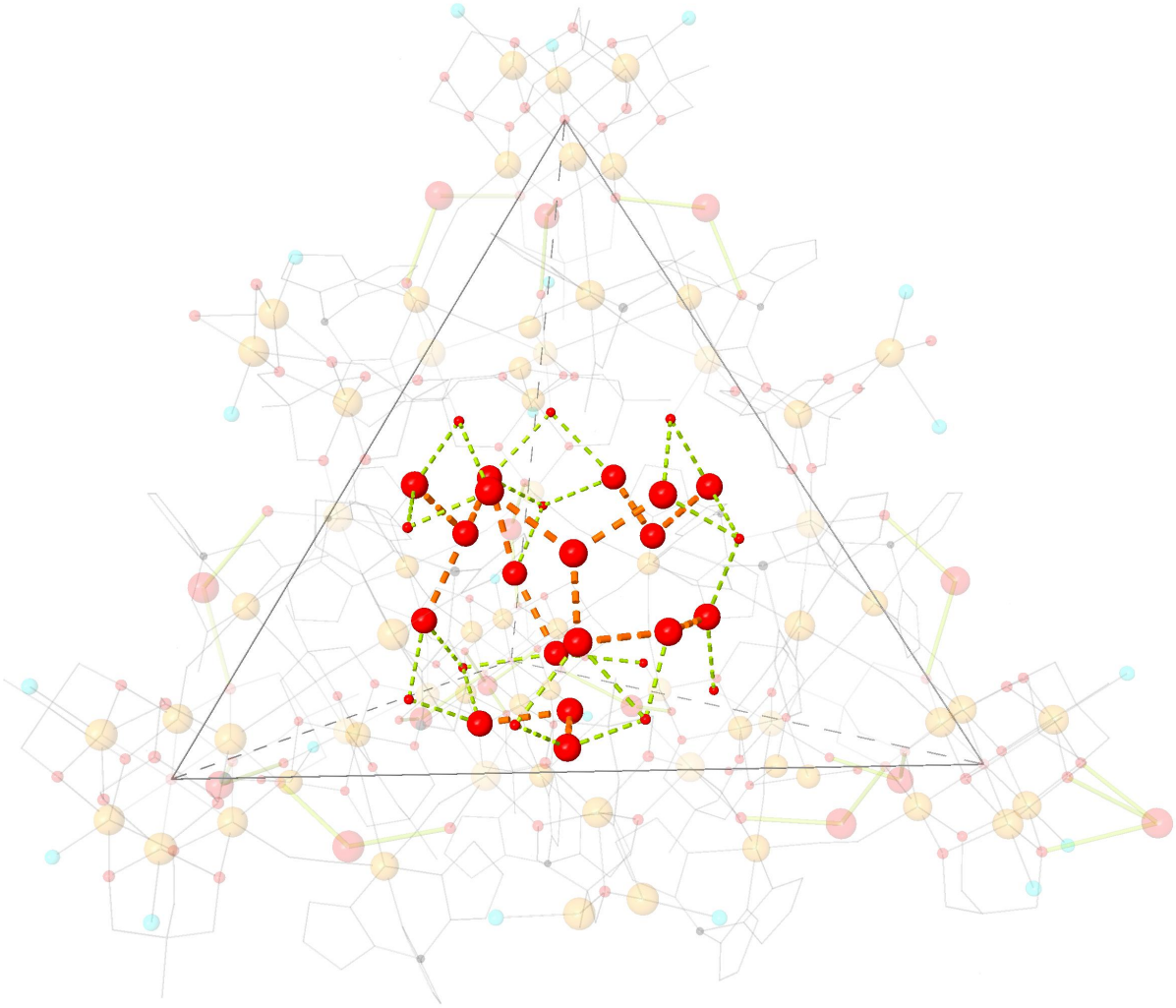

Figure S1. View of the water molecules hosted in the tetrahedron cavity. Colour code: orange, yellow and brown (Fe), red (O), cyan (Cl) and grey (C, B and N). Hydrogen atoms have been omitted for clarity. Dotted lines indicate H-bonds: orange (within the water motif) and green (involving an oxygen atom from the cage).

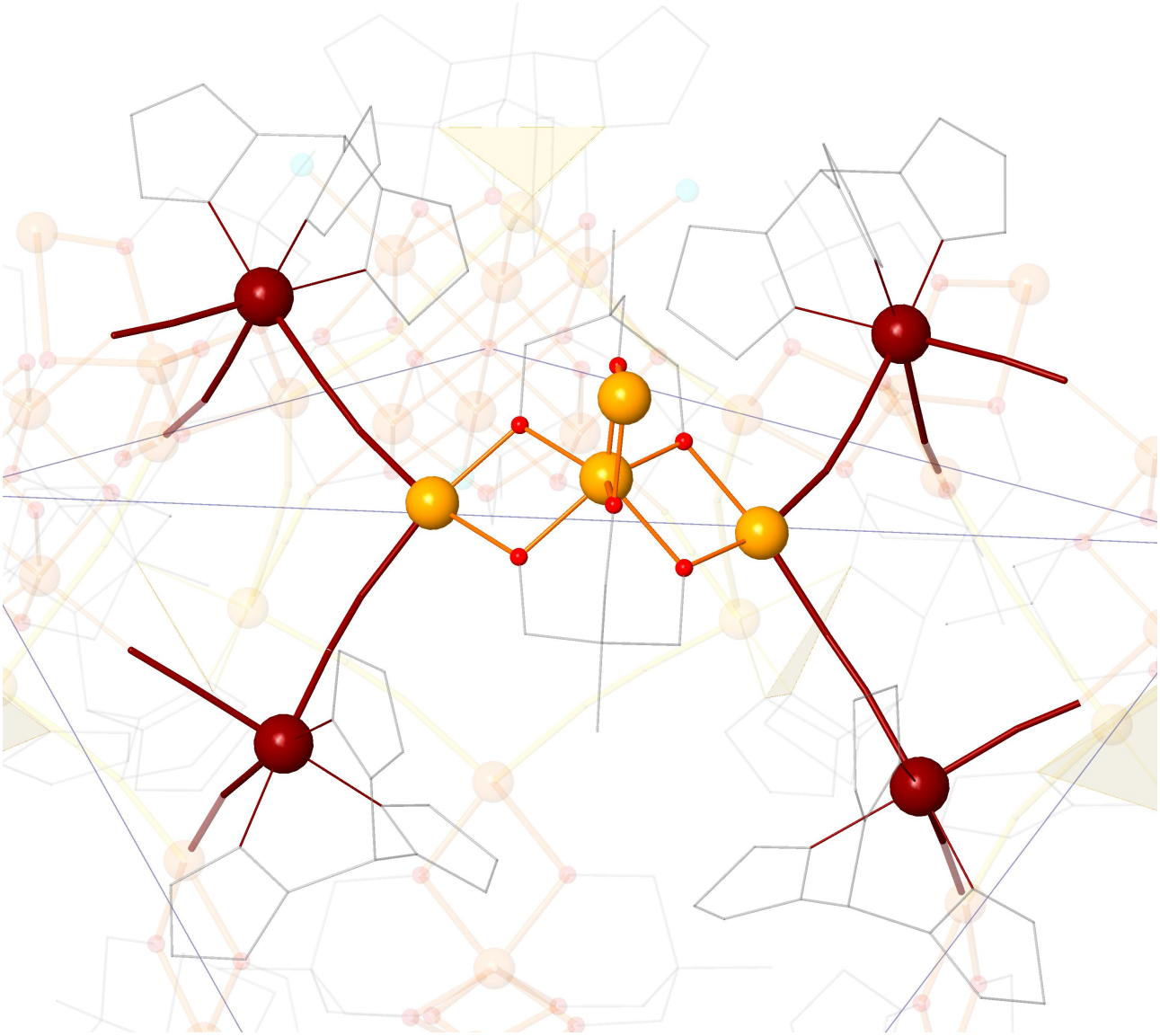

Figure S2. Representation of the {Fe_4} star-like subunit in **1** and of its connectivity with the {FeTp} units. Colour code: orange, yellow and brown (Fe), red (O), cyan (Cl) and grey (C, B and N). Hydrogen atoms have been omitted for clarity.

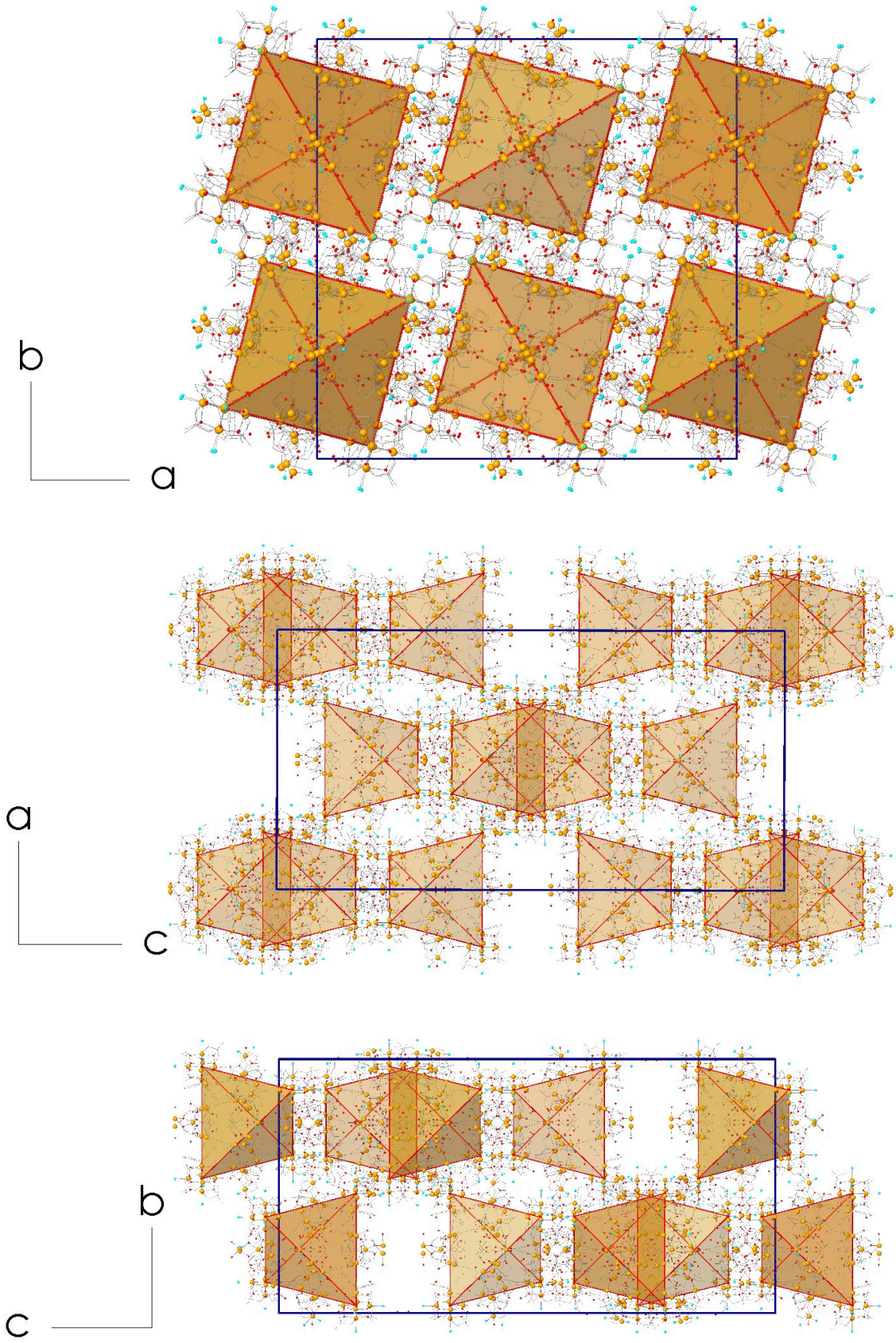

Figure S3. Crystal packing of **1** along the crystallographic *a* (a), *b* (b) and *c* (c) axes with a polyhedral view of the {Fe_{60}} tetrahedral cages. Colour code: light orange (Fe), red (O), cyan (Cl) and grey (C, B and N). Hydrogen atoms have been omitted for clarity.

Table S1. Selected bond distances (Å) and angles (°) in **1**

{Fe_6}	Fe—O	2.05 [1.96(1) – 2.32(1)]	X–Fe–X (X: Cl, N, O)	89.6 [80.3(3) – 100.4(4)]
	Fe—N	2.03 [2.00(2) – 2.05(1)]	Fe–(μ_6-O)–Fe	89.9 [89.2(5) – 91.6(5)]
	Fe—Cl	2.2 [2.263(3) – 2.287(7)]		
{Fe_4}*	Fe—O	2.0 [1.91(2) – 2.16(2)]	Fe–Fe–Fe	119.0 [100.1(3) – 132.2(2)]
	Fe—N	2.02 [1.99(2) – 2.06(2)]		
{FeTp}	Fe—C	1.85 [1.79(3) – 1.92(2)]	X–Fe–X (X: C, N)	89 [72(1) – 101(1)]
	Fe—N	1.99 [1.85(2) – 2.15(4)]	Fe–C–N	177 [174(1) – 179(2)]
			C–N–Fe(∈{Fe_6}/{Fe_4})	163 [152.5(1) – 171(2)]

**The values of the distances and angles around the peripheral iron atoms (Fe24, Fe34, Fe54 and Fe72) have been excluded from the analysis because of the uncertainty on the environment for these atoms.*

Table S2. BVS calculations[1–3]

{Fe_6}	Calc. for Fe(II)	Calc. for Fe(III)	{Fe_4}*	Calc. for Fe(II)	Calc. for Fe(III)
Fe1	2,73	2,89	Fe21	2,69	2,89
Fe2	2,76	2,92	Fe22	3,13	3,26
Fe3	2,82	2,99	Fe23	2,69	2,89
Fe4	2,76	2,90			
Fe5	2,72	2,85	Fe31	2,83	3,04
Fe6	2,72	2,85	Fe32	3,09	3,22
Fe7	2,78	2,92	Fe33	2,82	3,03
Fe8	2,73	2,88			
Fe9	2,70	2,86	Fe51	2,84	3,05
Fe10	2,71	2,85	Fe52	3,05	3,17
Fe11	2,75	2,89			
Fe12	2,73	2,87	Fe70	2,75	2,96
			Fe71	2,97	3,09

**The values of the distances around the peripheral iron atoms (Fe24, Fe34, Fe54 and Fe72) have been omitted from the calculations because of the uncertainty on the environment for these atoms.*

1 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B*, 1985, **41**, 244–247.

2 N. E. Brese and M. O'Keeffe, *Acta Crystallogr., Sect. B*, 1991, **47**, 192–197.

3 M. O'Keeffe and N. E. Brese, *Acta Crystallogr., Sect. B*, 1992, **48**, 152–154.

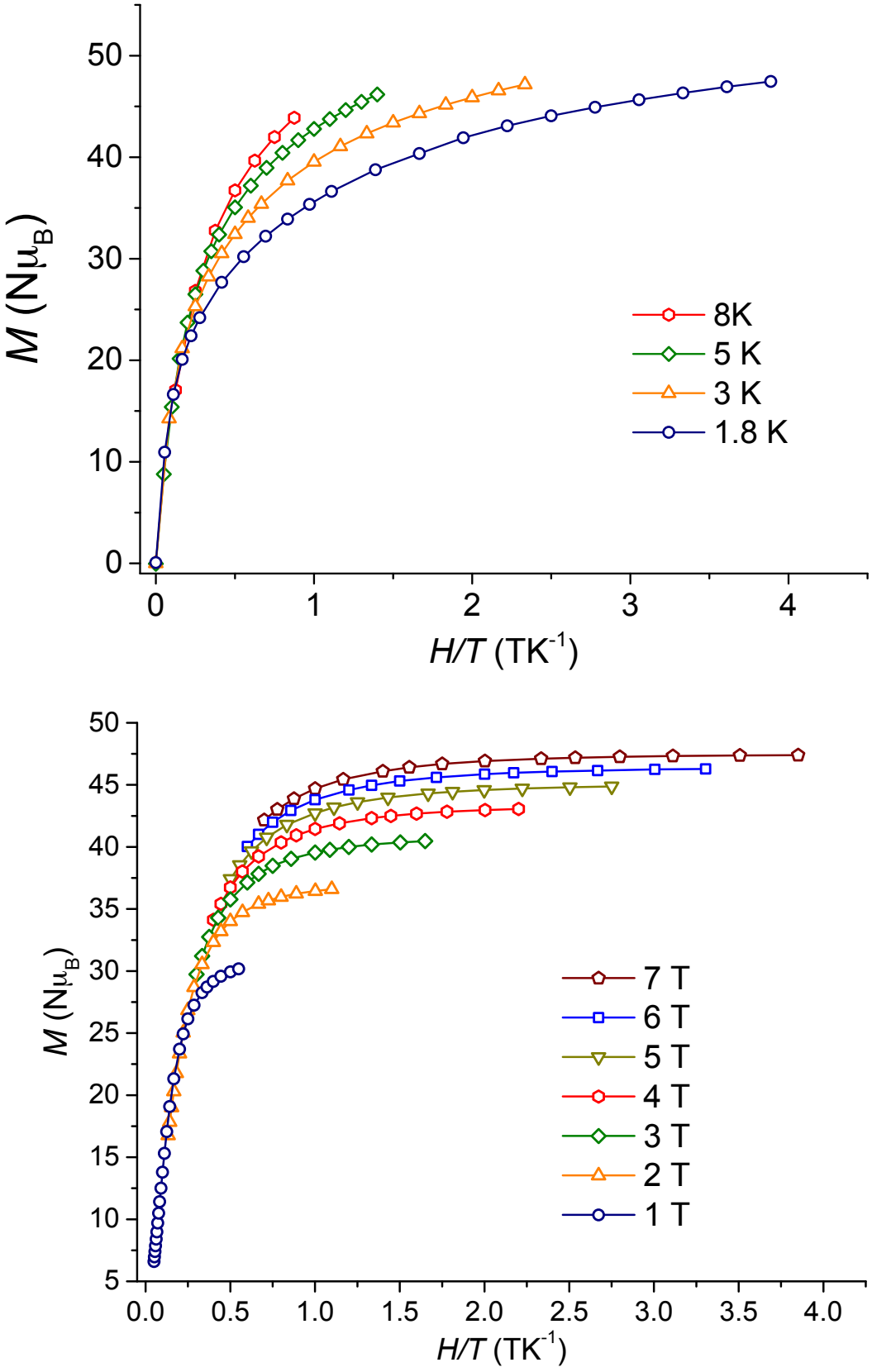

Figure S4. Field dependence of the magnetization of **1** at 1.8, 3.0 and 5.0 K; isothermal and isofield reduced magnetization of **1**.

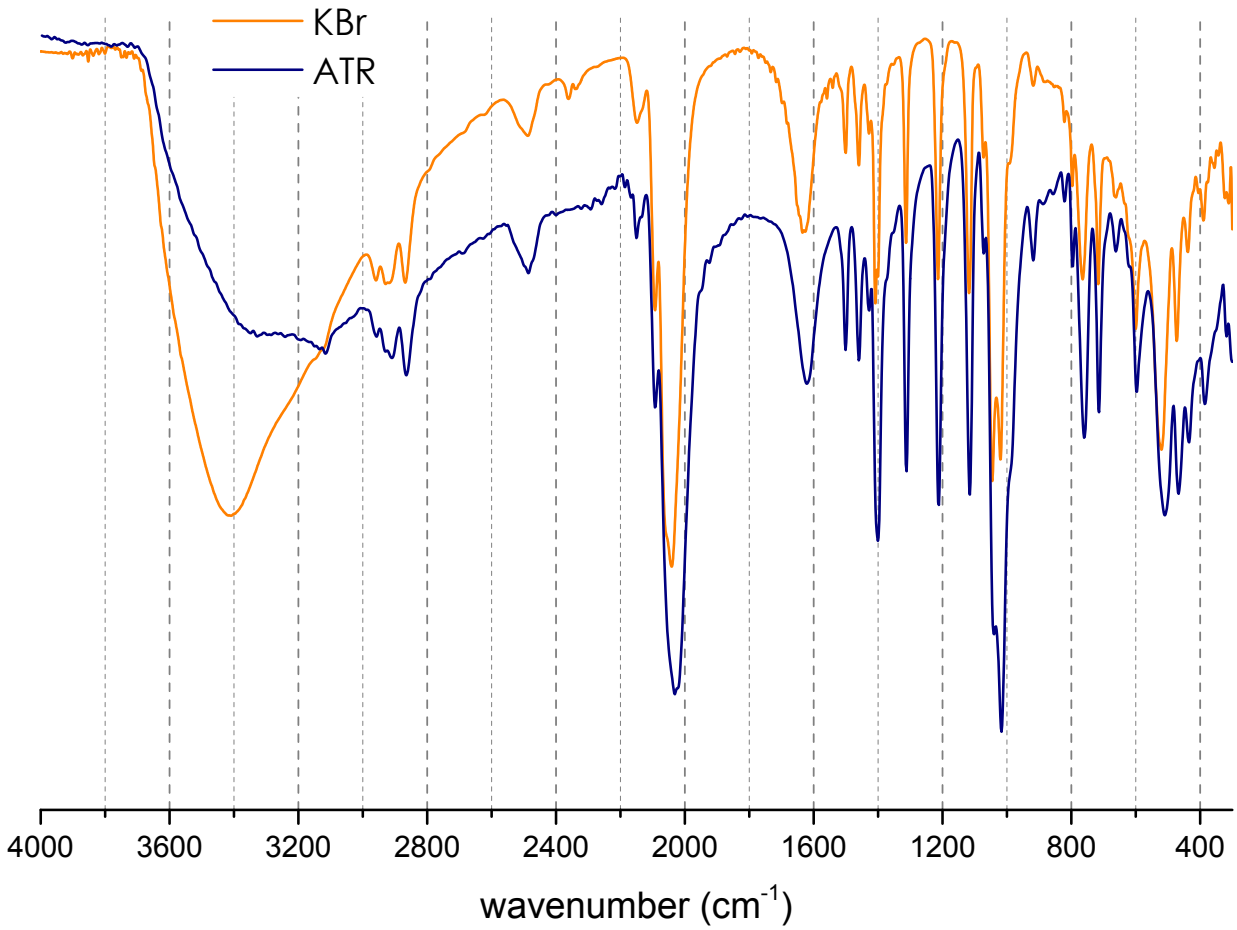

Figure S5. FT-IR spectra of **1** obtained by ATR (blue) and on KBr pellet (orange).

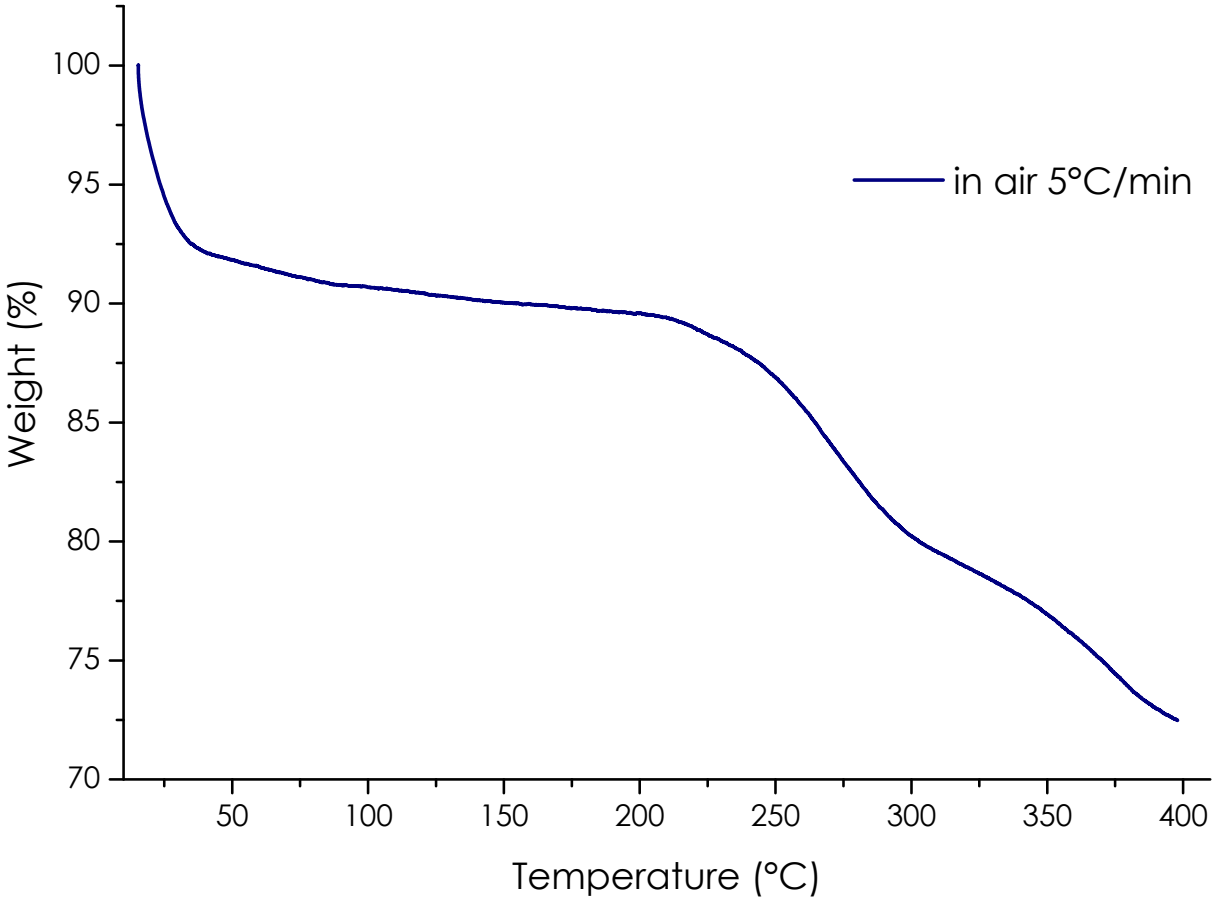

Figure S6. Thermogravimetric analysis of **1** in air at a heating rate of 5 °C/min.