A new class of 3-D porous framework: \([\text{Ln(H}_2\text{O)}_n]^{3+}\) ions act as pillars between \(\pi\)-stacked and H-bonded sheets of \((m-\text{BDTH})^-\) organic anions in \([\text{Ln(H}_2\text{O)}_n](m-\text{BDTH})_3\cdot9(\text{H}_2\text{O})\) (Ln = Pr, n = 9; Ln = Gd, n = 8).

George E. Kostakis, a Ghulam Abbas, a Christopher E. Anson a and Annie K. Powell a
**Fig. S1** The three dimensional framework of compound 1, viewed down the $a$-axis (left) and down the $b$-axis (right), showing the H-bonding between the coordinated waters and the organic anions. Pr purple, O red, N blue, C grey. The lattice water molecules are omitted for clarity.
**Fig. S2** Hydrogen-bonding between a \([\text{Pr(OH}_2)_9]^{3+}\) pillar and \((m\text{–BDTH})^-\) anions from the two adjacent organic layers in 1.

**Fig. S3** A hydrogen-bonded layer in the structure of 2 showing the lattice waters between the \([\text{Gd(OH}_2)_9]^{3+}\) cationic pillars. Gd green, O red, H pale grey. In the structure of 2, crystal waters also associate to form two independent helical chains. One of these can best be described as ‘\((\text{H}_2\text{O})\text{··}-(\text{H}_2\text{O})\text{··}-(\text{H}_2\text{O})\text{··}-(\text{H}_2\text{O})\text{··}-(\text{H}_2\text{O})\text{··}\)’ in which hydrogen bonds highlighted in blue and pink, while the second water infinite tape is highlighted in orange.
Fig. S4 Thermogravimetric data for compound 2
Fig. S5 X-ray powder patterns for compound 2