Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Neodymium 1D systems: targeting new sources for field-induced slow magnetization relaxation

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1. Experimental Section

1.1 Physical Measurements

All the reagents were commercially available and used as received. The melting points were determined with an electrically heated apparatus. C, H, N elemental analyses were obtained with a CHNS-O analyzer flash-EA-1112 series. The IR spectra of compounds were recorded on Perkin ELMER FTIR spectrometer in the range 4000-400cm^{-1}. Thermogravimetric analysis (TGA) data were collected on a NetzschTG-209 instrument. Single crystal structural X-ray diffraction was carried out on a Bruker's Apex-II CCD diffractometer using Mo Kα (λ=0.71069Å) at room temperature. The X-ray powder diffraction (XRPD) measurements were recorded on a Rigaku miniflex X-ray diffractometer with Cu Kα radiation. Magnetic susceptibility measurements were carried out between 2-300 K in a SQUID Quantum Design Magnetometer, model MPMP at the "Unitat de Mesures Magnètiques (Universitat de Barcelona)". Two different magnetic fields were used for each sample in the range of 1.8 - 300 K of 5000 G for **1** and 3000 G for **2**, respectively. Pascal's constants were used to estimate the diamagnetic corrections for the compounds.

1.2 Synthesis of $\{[Nd(\mu_2\text{-}L1)_3(H_2O)_2].C_2H_3N\}_n$ (1)

To a solution of $Nd(NO_3)_2.6H_2O$ (1 mmol, 0.438 g) in 10 mL of water, 2-3 drops of NaOH 0.1 M were added. Then, a suspension of L1 (1 mmol, 0.21 g) in 20 mL of acetonitrile was added drop wise. The mixture was stirred at room temperature for 10 minutes and the resulting solution was allowed to slowly evaporate to give light pink crystals within 1-2 week (79% yield). M.p.>300 ºC. Anal. Calcd for $\mathbf{C_{23}H_{16}N_7O_{20}Nd}$ (%): C, 32.01; H, 1.85; N, 11.46; Found: C, 32.14; H, 1.81; N, 11.30. IR (cm^{-1}) selected bonds: υ = 3589 (b) (O-H), 3089 (m) (Ar-H), 1643(w) $(COO^-)_{asy}$, 1539 (s) $(COO^-)_{sy}$, 1410 (w) (C=C), 1348 (m) (N-O), 586 (w) (M-O).

1.3 Synthesis of $[Nd(\mu_2\text{-}L2)(L2)(CH_3COO)(H_2O)_2]_n$ (2)

To a solution of $Nd(CH_3COO)_3{\cdot}H_2O$ (0.339 g, 1 mmol) in 10 mL of water, 2-3 drops of NaOH 0.1 M were added. Then, a suspension of L2 (1 mmol, 0.21 g) in 20 mL of acetonitrile was added drop wise. The mixture was stirred for 10 minutes before transferring to a 40 mL Teflon-lined stainless steel vessel, which was sealed and heated at 120 ºC for 24 h. After that the reaction system was slowly cooled to room temperature. Light Pink crystals were filtered off and dried in air. (77% yield). M.p.>300 ºC. Anal. Calcd for **$C_{16}H_{13}N_4O_{16}Nd$** (%): C, 29.03; H, 1.95; N, 8.46; Found: C, 29.05; H, 1.81; N, 8.30. IR (cm^{-1}) selected bonds: υ = 3578 (b) (O-H), 3110 (m) (Ar-H), 1632 (s) $(COO^-)_{asy}$, 1536 (s) $(COO^-)_{sy}$, 1404 (m) (C=C), 1347 (m) (N-O), 592 (m) (M-O).

2. X-ray crystallography

X-ray data of compounds **1** and **2** were collected by CCD diffractometer and processed by SAINT. Lorentz and polarization effects and empirical absorption corrections were applied using SADABS from Bruker. The structures were solved by direct methods, using SIR-92[1] and refined by full-matrix least squares refinement methods[2] based on F^2, using SHELX-97. The hydrogen atoms of water molecules were located from the difference Fourier synthesis and were refined isotropically with distance of 0.82 Å with U_{iso} values 1.2 times that of their carrier oxygen atoms. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed geometrically with their U_{iso} values 1.2 times of phenylene carbons and 1.5 times of terminal methyl carbons of acetonitrile solvent and acetate groups. All calculations were performed using Wingx package.[3] Crystal data as well as details of data collection and refinement for the complexes are summarized in Table S1.

References

(1) Altomare, A.; Cascarano, G.; Giacovazzo, C. ; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343-350.

(2) Sheldrick, G. M. *Acta Cryst A*. **2008**, *A64*, 112-122.

(3) Farrugia, L. J. *J. Appl. Cryst*. **1999**, *32*, 837-838.

Table S1. Crystallographic data for compounds **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{23}H_{16}N_7NdO_{20}$	$C_{16}H_{13}N_4NdO_{16}$
Formula weight	854.67	661.54
Temperature	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P\ 2_1/n$	$P2_1$
Unit cell dimensions	a = 9.4980(2) Å, α = 90°. b = 15.709(3) Å, β = 90.837(8)° c = 21.263(3) Å, γ = 90°.	a = 17.5380(5) Å, α = 90° b = 6.9480(2) Å, β= 101.684(12)° c = 19.1470(6) Å, γ = 90°
Volume	3172.19(10) $Å^3$	2284.80(12) $Å^3$
Z	4	4
Density (calculated)	1.790 Mg/m^3	1.923 Mg/m^3
Absorption coefficient	1.735 mm^{-1}	2.362 mm^{-1}
F(000)	1692	1300
Crystal size	0.12 x 0.08 x 0.05 mm^3	0.11 x 0.08 x 0.06 mm^3
Theta range for data collection	1.61 to 36.86°.	1.44 to 26.39°.
Index ranges	-16<=h<=10, -26<=k<=24, -35<=l<=35	-21<=h<=21, -8<=k<=8, -23<=l<=23
Reflections collected	62474	18573
Independent reflections	15887 [R(int) = 0.0358]	8187 [R(int) = 0.0251]
Completeness to theta	99.5 %	99.5 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7472 and 0.6299	0.7454 and 0.6179
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	15887 / 4 / 473	8187 / 9 / 693
Goodness-of-fit on F^2	1.022	0.702
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.0748	R1 = 0.0233, wR2 = 0.0575
R indices (all data)	R1 = 0.0887, wR2 = 0.0900	R1 = 0.0255, wR2 = 0.0594
Largest diff. peak and hole	1.428 and -0.634 e.$Å^{-3}$	0.798 and -0.451 e.$Å^{-3}$
CCDC number	**1051022**	**1051023**

3. Results of X-ray crystallography

3.1 $\{[Nd(\mu_2\text{-}L1)_3(H_2O)_2]\cdot C_2H_3N\}_n$ (1)

ORTEP of **1** is shown in Fig. S1. Each Nd^{III} ion in **1** has a bicapped trigonal prismatic geometry (Fig. S2(a)). The six sites are occupied by carboxylate oxygen atoms (O13$^{\#1}$, O14, O15$^{\#2}$, O16, O17$^{\#1}$ and O18 (#1: -x+1,-y,-z, #2: -x+2,-y,-z)) of **L1** and two sites by oxygen atoms (O1W and O2W) of water molecules, forming twisted ribbons along *a* axis. Selected bond distances and angles are collected in Table S2.

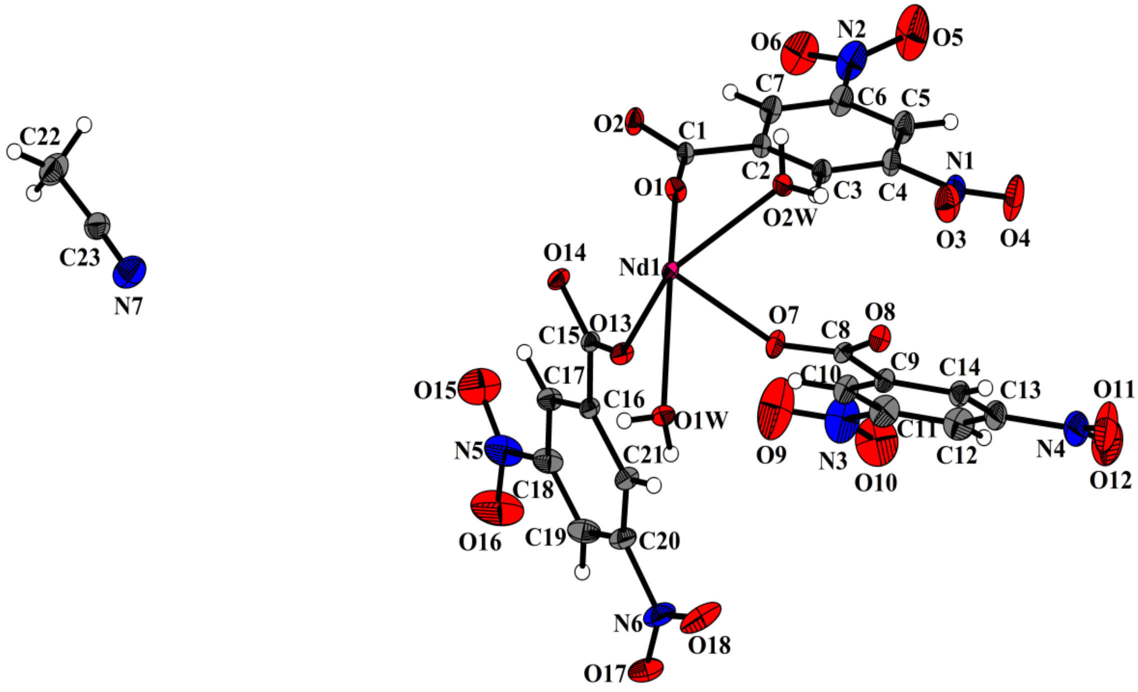


Fig. S1. ORTEP showing asymmetric unit of compound **1**, with 30 % probability.

Table S2. Selected bond lenghts (Å) and angles (°) in compound **1**.

Nd(1)-O(1)	2.4186(16)
Nd(1)-O(7)	2.3840(18)
Nd(1)-O(13)	2.4534(17)
Nd(1)-O(1W)	2.6140(18)
Nd(1)-O(2W)	2.5199(18)
O(7)-Nd(1)-O(1)	90.61(7)
O(7)-Nd(1)-O(13)	76.50(6)
O(1)-Nd(1)-O(13)	74.18(6)
O(7)-Nd(1)-O(2W)	71.68(7)
O(1)-Nd(1)-O(2W)	74.63(6)
O(13)-Nd(1)-O(2W)	134.59(7)
O(7)-Nd(1)-O(1W)	70.24(7)
O(1)-Nd(1)-O(1W)	145.22(6)
O(13)-Nd(1)-O(1W)	73.24(6)
O(2W)-Nd(1)-O(1W)	122.50(6)

There are strong intramolecular H-bonding interactions between two coordinated water molecules (O1W and O2W) forming linear chain along *a* axis, further supporting the 1D CP (Fig. S2(b)). Additionally, O1W water molecule is also showing H-bonding with oxygens of –NO_2 groups in *bc* plane forming 2-D, H-bonded network (Fig. S2(c)). This creates 1D channels along *a* axis which are filled by acetonitrile molecules which are held by H-bonding of N7 with O2W water molecules (Fig. S2(d)) and aromatic C4 carbon atoms. The methyl hydrogens of acetonitrile are H-bonded to oxygens of nitro groups (Table S3).

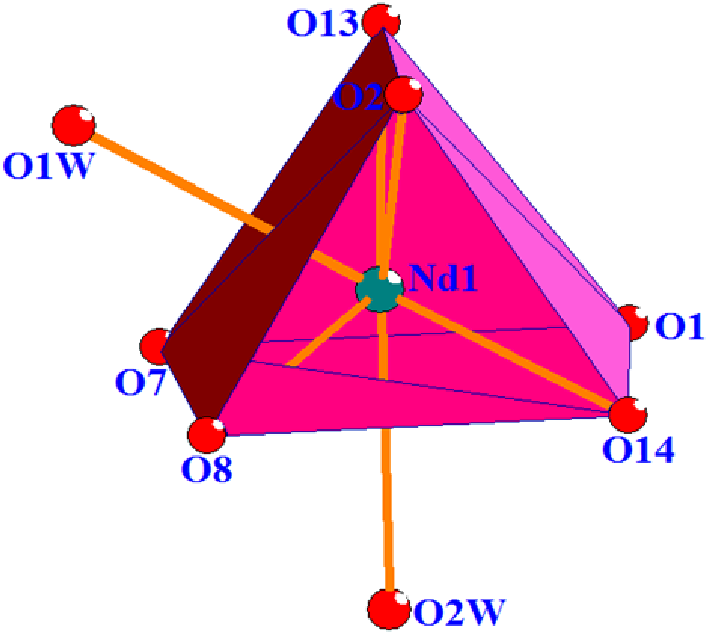


Fig. S2 (**a**) Trigonal bicapped geometry around Nd^{III} metal ion.

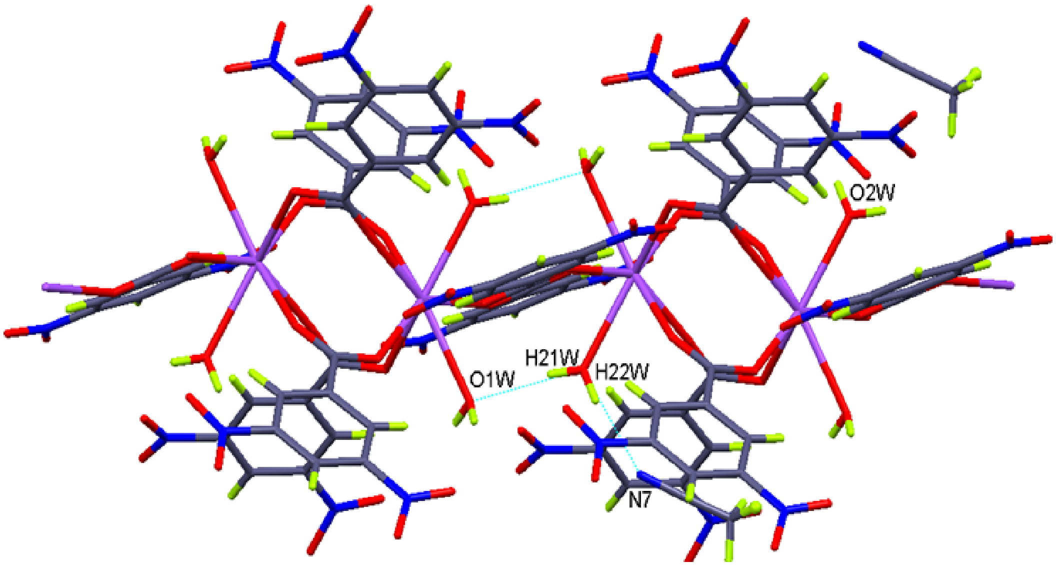


Fig. S2 (**b**) Coordination as well as H-bonded chain along *a* axis.

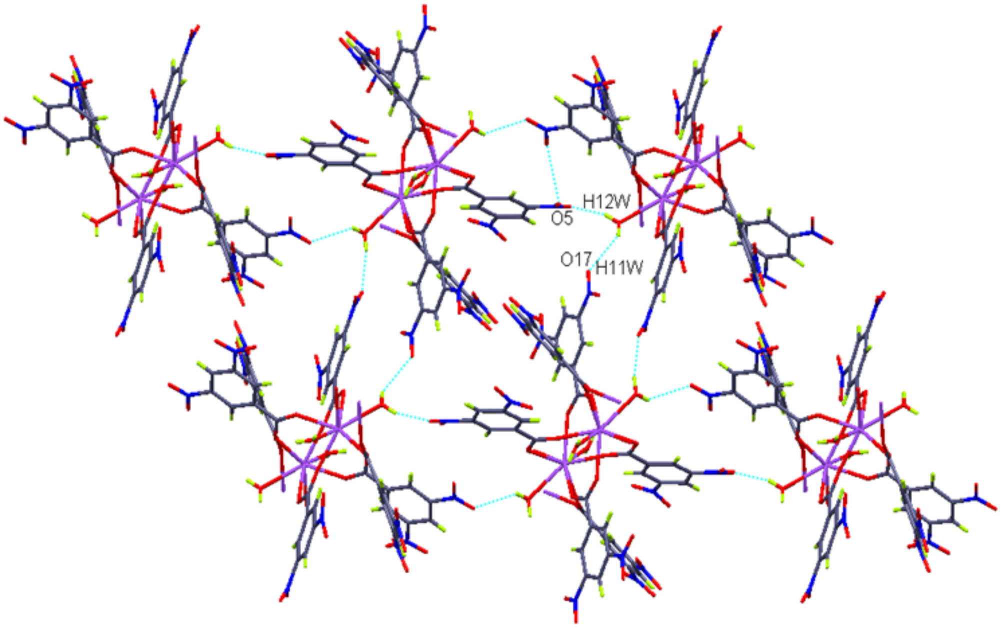


Fig S2 (**c**) 2D, H-bonded network between coordinated water O1W and oxygens of –NO_2 groups in *bc* plane with channels along *a* axis.

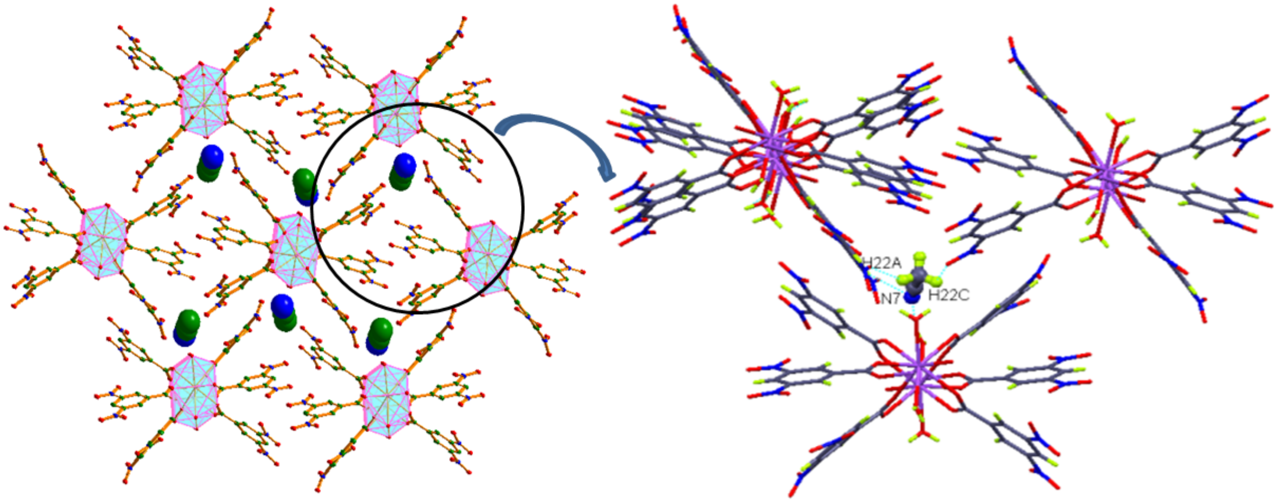


Fig. S2 (**d**) 2D H-bonded network with channels filled with acetonitrile molecules (expanded portion shows H-bonding interactions between solvent and the CP.)

Table S3. Hydrogen bond distances (Å) and angles (^{o}) for compound **1**

X-H···Y	**X···Y**	**H···Y**	**∠X-H···Y**
O2W-H21W···O8	3.134(3)	2.65(3)	120
O1W-H11W···O2^{1}	2.794(3)	2.40(3)	111
C22-H22B...O11^{1}	3.542(6)	2.73	143
O1W-H12W···O6^{2}	3.488(4)	2.76(3)	153
O1W-H12W···O5^{2}	2.939(5)	2.24(3)	147
O1W-H12W···N2^{2}	3.564(4)	2.81(3)	158
O2W-H21W···O1W^{3}	2.950(3)	2.15(2)	168
O1W-H11W···O3^{3}	3.359(4)	2.98(3)	111
O1W-H11W···O17^{4}	3.222(4)	2.57(3)	139
O2W-H22W···N7^{5}	2.809(4)	2.04(3)	159
O2W-H22W···O5^{6}	3.416(5)	2.96(3)	119
C22-H22A···O6^{7}	3.407(5)	2.57	146
C22-H22B···O16^{8}	3.223(6)	2.76	111
C22-H22C···O2^{9}	3.681(5)	2.99	132
C22-H22C···O17^{10}	3.204(5)	2.67	115
C22-H22C···O18^{10}	3.470(5)	2.81	126

(1) -x+1,-y,-z (2) x+1/2,-y-1/2,+z+1/2 (3) -x+2,-y,-z (4) -x+1/2+1,+y+1/2,-z+1/2
(5) x+1/2,-y+1/2,+z-1/2 (6) -x+1/2+1,+y+1/2,-z-1/2 (7) -x,-y,-z (8) x,+y+1,+z
(9) x-1,+y+1,+z (10) x-1/2,-y+1/2,+z+1/2

3.2 [Nd(μ_2-L2)(L2)(CH_3COO)(H_2O)$_2$]$_n$ (2)

ORTEP of **2** is shown in Fig. S3. Selected bond length and angles are collected in Table S4.

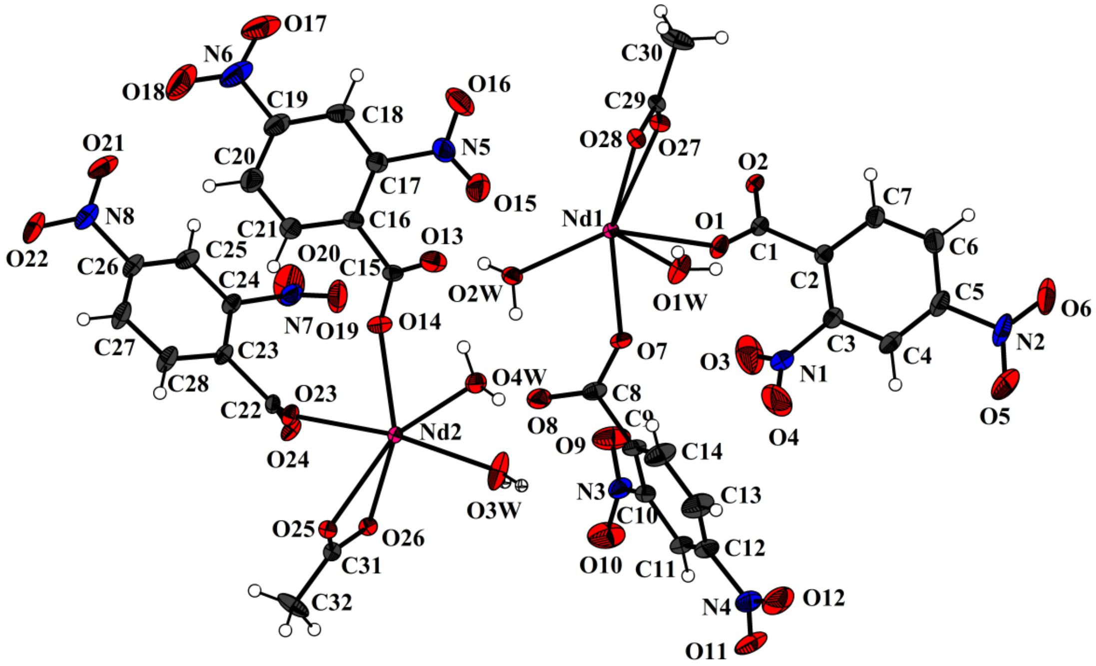


Fig. S3. ORTEP showing asymmetric unit of compound **2**, with 30 % probability

Table S4. Selected bond lenghts (Å) and angles (°) in compound **2**.

O(1)-Nd(1)	2.470(3)	O(7)-Nd(1)-O(2W)	69.78(11)
O(1W)-Nd(1)	2.469(4)	O(7)-Nd(1)-O(1W)	71.85(14)
O(2W)-Nd(1)	2.460(3)	O(2W)-Nd(1)-O(1W)	126.82(14)
O(3W)-Nd(2)	2.501(4)	O(7)-Nd(1)-O(1)	75.11(13)
O(4W)-Nd(2)	2.421(3)	O(2W)-Nd(1)-O(1)	133.25(13)
O(7)-Nd(1)	2.400(3)	O(1W)-Nd(1)-O(1)	65.81(11)
O(14)-Nd(2)	2.404(3)	O(7)-Nd(1)-O(27)	145.91(14)
O(23)-Nd(2)	2.518(3)	O(2W)-Nd(1)-O(27)	131.18(11)
O(25)-Nd(2)	2.536(3)	O(1W)-Nd(1)-O(27)	100.86(13)
O(26)-Nd(2)	2.629(3)	O(1)-Nd(1)-O(27)	71.71(12)
O(27)-Nd(1)	2.591(3)	O(7)-Nd(1)-O(28)	142.80(13)
O(28)-Nd(1)	2.625(3)	O(2W)-Nd(1)-O(28)	131.66(11)
		O(1W)-Nd(1)-O(28)	71.38(12)
		O(1)-Nd(1)-O(28)	94.82(12)
		O(27)-Nd(1)-O(28)	49.46(9)
		O(14)-Nd(2)-O(4W)	69.07(12)
		O(14)-Nd(2)-O(3W)	115.76(16)
		O(4W)-Nd(2)-O(3W)	70.82(14)
		O(14)-Nd(2)-O(23)	72.89(11)
		O(4W)-Nd(2)-O(23)	140.89(11)
		O(3W)-Nd(2)-O(23)	136.86(12)
		O(14)-Nd(2)-O(25)	135.90(12)
		O(4W)-Nd(2)-O(25)	135.42(13)
		O(3W)-Nd(2)-O(25)	107.83(15)
		O(23)-Nd(2)-O(25)	71.02(11)
		O(14)-Nd(2)-O(26)	135.63(11)
		O(4W)-Nd(2)-O(26)	145.94(12)
		O(3W)-Nd(2)-O(26)	76.11(13)
		O(23)-Nd(2)-O(26)	71.53(10)
		O(25)-Nd(2)-O(26)	49.73(10)

There are two crystallographically independent molecules present in the unit cell of compound **2**. The geometry around Nd^{III} ion is tricapped trigonal prismatic (Fig. S4(a)) by coordinating with **L2** to form 1D coordination polymer along *b* axis (Fig. S4(b)). In each one of crystallographically independent chains, intramolecular H-bonding interactions among coordinated water molecules, methyl groups, aromatic rings and –COO, –NO$_2$ groups, further support the propagation of 1D CP along *b* axis (Fig. S4(c)). Two crystallographic independent 1D chains, in turn are connected to each other through intermolecular H-bonding interactions involving coordinated waters and oxygens of –COO and –NO$_2$ groups (Fig. S4(d). These interactions lead to form a 2D network, further extending in *bc* plane, having various supramolecular synthons like **R_4^2(8)**, **R_1^1(6)**, **R_2^1(6)**, R_1^2**(7)** and **R_1^2(4)** (Fig. S4(e)). Weak H-bonding interactions between –NO$_2$ groups and protons of aromatic rings extend the network to 3D as shown in *ac* plane (Fig. S4(f) (Table S5).

The coordination number of Nd^{III} ion, coordination modes of ligand, Point symbol and topology, dimensionality, M···M distances and chirality of compounds **1** and **2** are listed in Table S7.

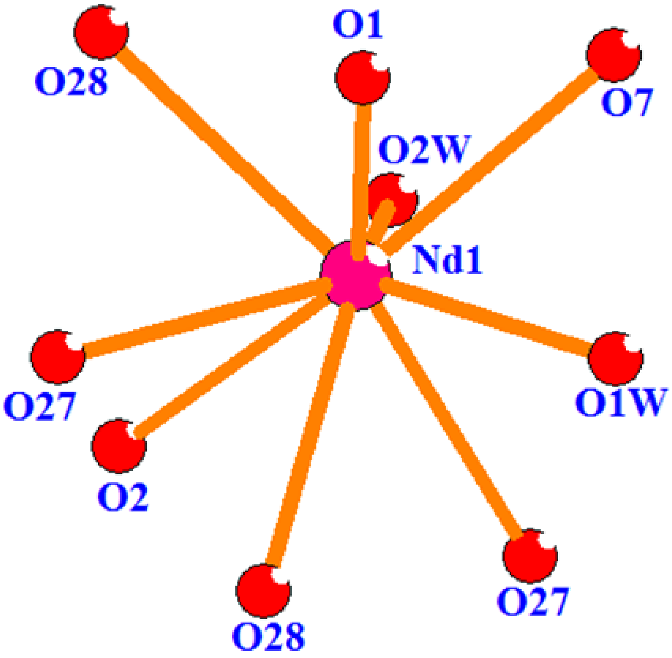


Fig. S4 (**a**) Trigonal prismatic tricapped geometry around Nd^{III} metal ion.

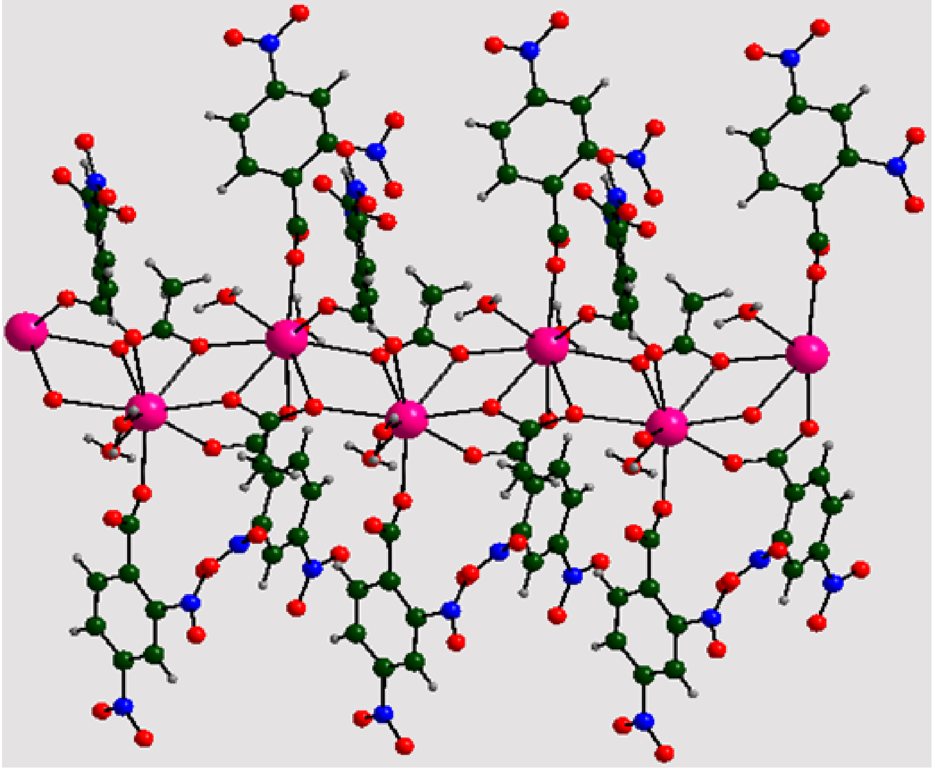


Fig. S4 (**b**) Molecular structure of 1-D polymeric compound (**2**) along *b* axis (only one crystallographically independent chain is shown).

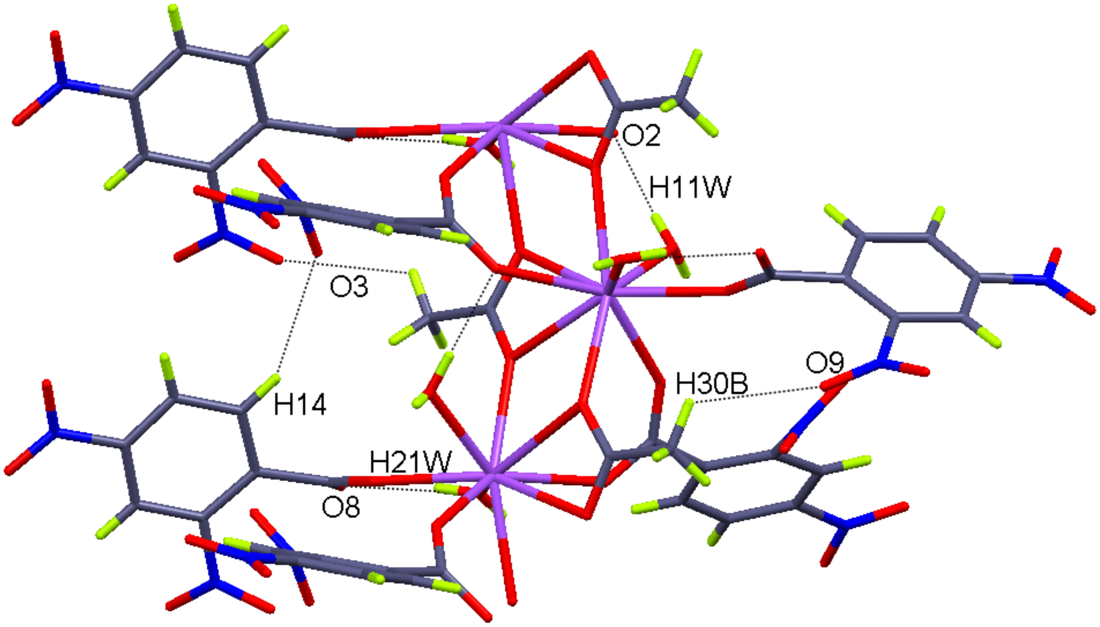


Fig. S4 (**c**) Intramolecular H-bonding interactions among coordinated water molecule, –COO, –NO_2 groups, protons of methyl group and aromatic ring. (only one crystallographically independent chain is shown).

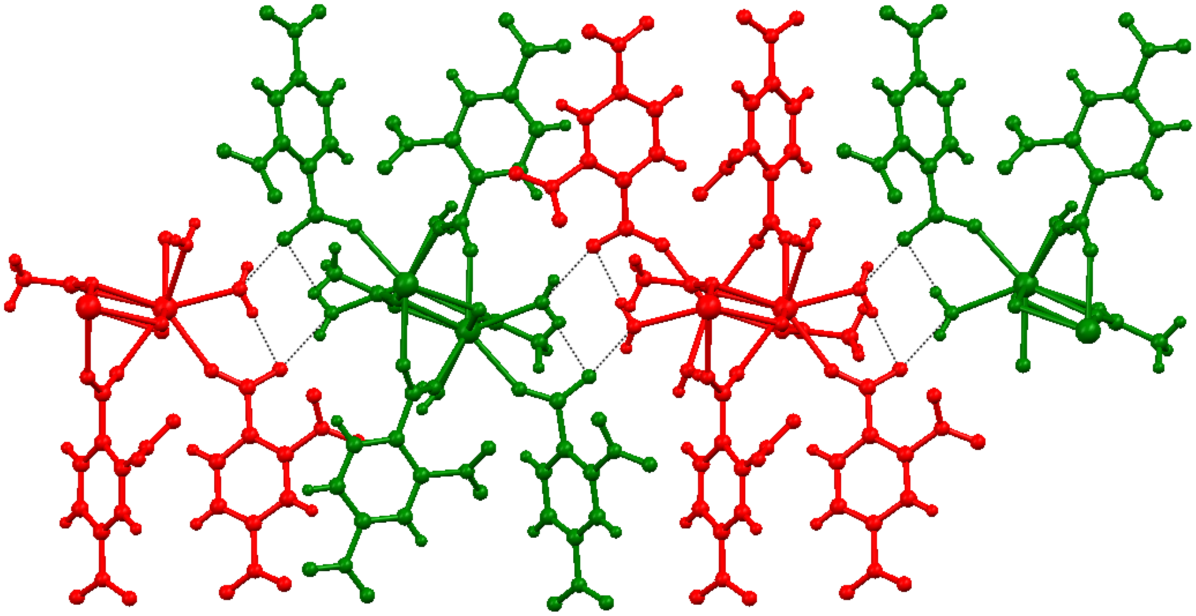


Fig. S4 (**d**) H-bonding interactions between two crystallographic independent 1D chains (red and green color) extending the network further in *bc* plane.

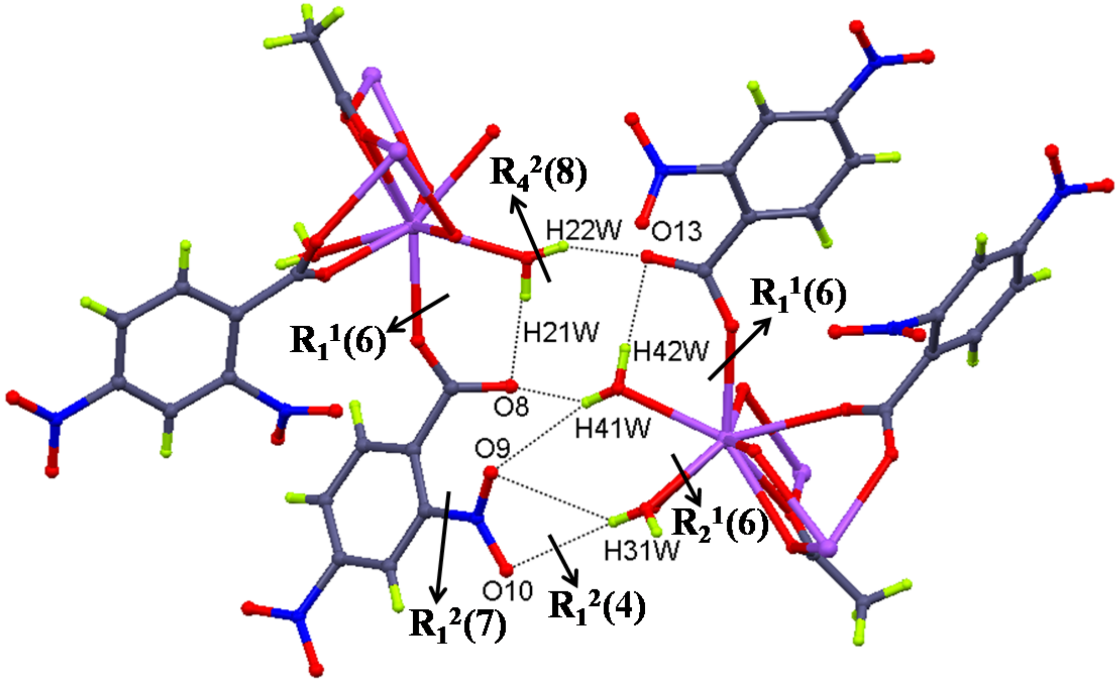


Fig. S4 (**e**) Zoomed in H-bonded area from Fig. S4(d) to show H-bonding interactions between two crystallographic independent chains forming various supramolecular synthons.

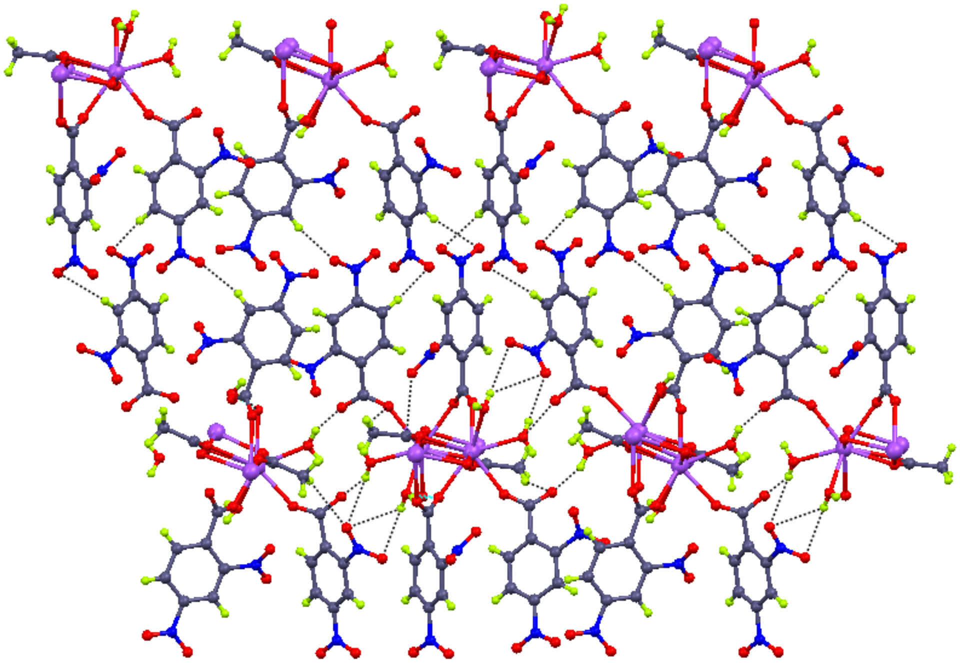


Fig. S4 (f) Weak H-bonding interactions between –NO_2 groups and protons of aromatic rings forming 3D network (shown in *ac* plane).

Table S5. Hydrogen bond distances (Å) and angles (°) for compound **2**

X-H···Y	X···Y	H···Y	∠X-H···Y
O2W-H21W···O4W	3.360(5)	2.93(5)	115
O2W-H21W···O7	2.781(4)	2.39(4)	110
O2W-H21W···O8	2.720(4)	1.91(3)	169
O2W-H22W···O13	2.833(6)	2.08(5)	153
O3W-H31W···N3	3.721(7)	2.96(6)	158
O3W-H31W···O9	3.322(7)	2.71(7)	134
O3W-H31W···O10	3.383(7)	2.58(5)	172
O4W-H41W···O8	2.733(6)	2.00(6)	149
O4W-H41W···O9	3.167(6)	2.63(5)	125
O4W-H42W···O2W	3.360(5)	2.89(6)	118
O4W-H42W···O13	2.781(5)	1.96(4)	172
O4W -H42W···O14	2.736(5)	2.31(5)	113
O1W-H11W···O2^1	2.725(5)	1.94(5)	162

O3W-H32W···O23^{2}	2.737(6)	1.94(5)	161
C32-H32C...O8^{2}	3.699(8)	2.78	160
C32-H32B...O13^{2}	3.521(8)	2.65	151
C32-H32A...O14^{3}	3.474(8)	2.63	146
C32-H32A...O15^{3}	3.479(7)	2.82	126
C30-H30B...O4W^{4}	3.567(8)	2.99	120
C30-H30B...O7^{4}	3.761(9)	2.92	147
C30-H30B...O9^{4}	3.245(7)	2.69	117

(1) x,+y+1,+z (2) -x+1,+y-1/2,-z+2 (3) -x+1,+y+1/2,-z+2 (4) -x+1,+y+1/2,-z+1

4. Thermo gravimetric analysis

Thermal decomposition of these compounds were carried out under nitrogen at heating range of 10 deg min^{-1}.The TGA curve of (**1**) (Fig. S5a) shows that at 109 °C temperature, the loss of 5.8 % (calcd 4.8 %) weight due to loss of acetonitrile solvent molecule from lattice (wt left 94.2%, calcd 95.2 %) with endothermic peak of -2.25 W/g. After that at 320 °C, loss of coordinated water molecules is taking place (wt 90.78 %, calcd 90.99 %) and endothermic peak is observed of -2.51 W/g. The complex is stable up to 406 °C and decomposition of the parent complex, with explosion and a sharp exothermic peak of 3.31 W/g, is observed at 409 °C.

Compound **2** (Fig. S5b) is stable up to 68 °C, after that it loses 5.44 % weight of two coordinated water molecules (weight left 95.49 %, calcd 95.67 %) and at 215 °C it loses 8.9 % weight due to one acetate anion (weight left 84.34 %, calcd 84.37 %), beyond that it is stable up to 244 °C where it finally decomposes with explosion giving a sharp exothermic peak of 0.343 W/g.

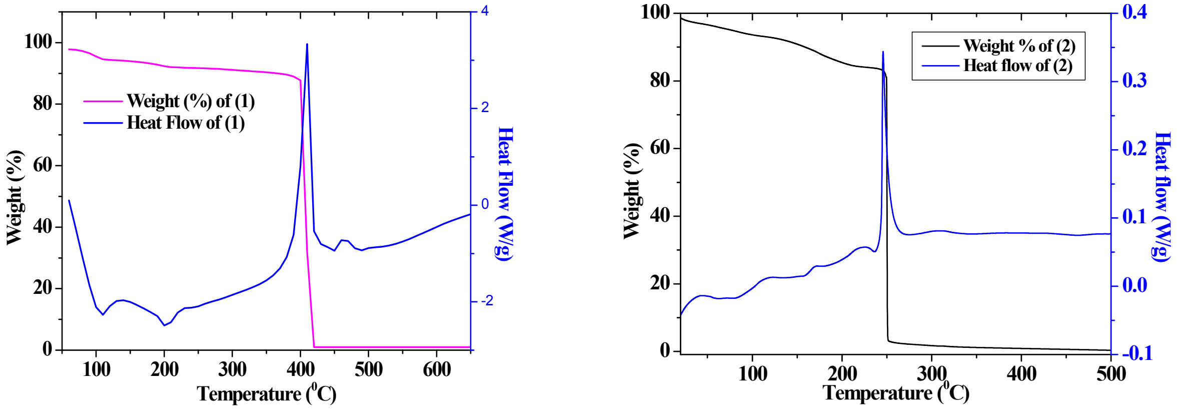


Fig. S5. TGA graph of (a) compound **1** and (b) compound **2**.

5. IR spectroscopy

In both complexes of Nd^{III} ions**,** symmetric and anti symmetric –OH stretching bands appears as broad bands in the region of 3575-3589 cm^{-1}**.** The C-H and C-C vibrations belonging to the aromatic rings are found around 3082-3112 cm^{-1} and 1404-1412 cm^{-1}. The characteristic peaks of asymmetric and symmetric stretches of COO^{-} are found in the regions 1630-1643 cm^{-1} and 1535-1539 cm^{-1} respectively. The complexes contain aromatic N-O stretch in the region of 1346-1349 cm^{-1} and weak bands around 583-592 cm^{-1} are assigned to M-O vibrations (Fig. S6, Table S6).

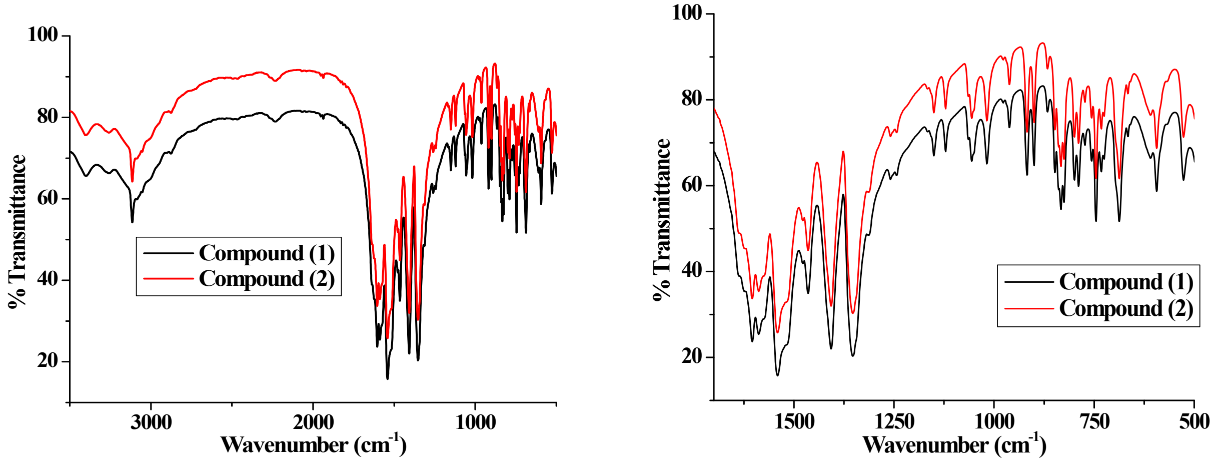


Fig. S6. IR spectra of compounds **(1)** and **(2)**.

Table S6. IR frequencies of main functional groups

Code	O-H	$(COO^-)_{asy}$	$(COO^-)_{sy}$	N-O	M-O
1	3589	1643	1539	1348	586
2	3578	1632	1536	1347	592

6. PXRD studies

The PXRD patterns of compounds (**1**) and (**2**) are similar to the simulated ones from their crystal structure (Fig. S7 and S8) indicating the homogeneity of the samples.

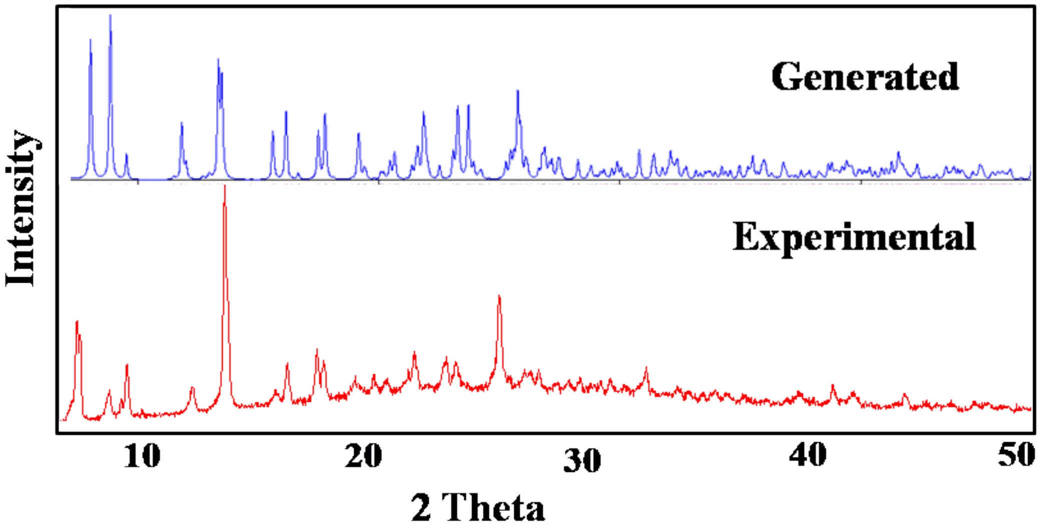


Fig. S7. Showing generated and experimental PXRD patterns of compound (**1**)

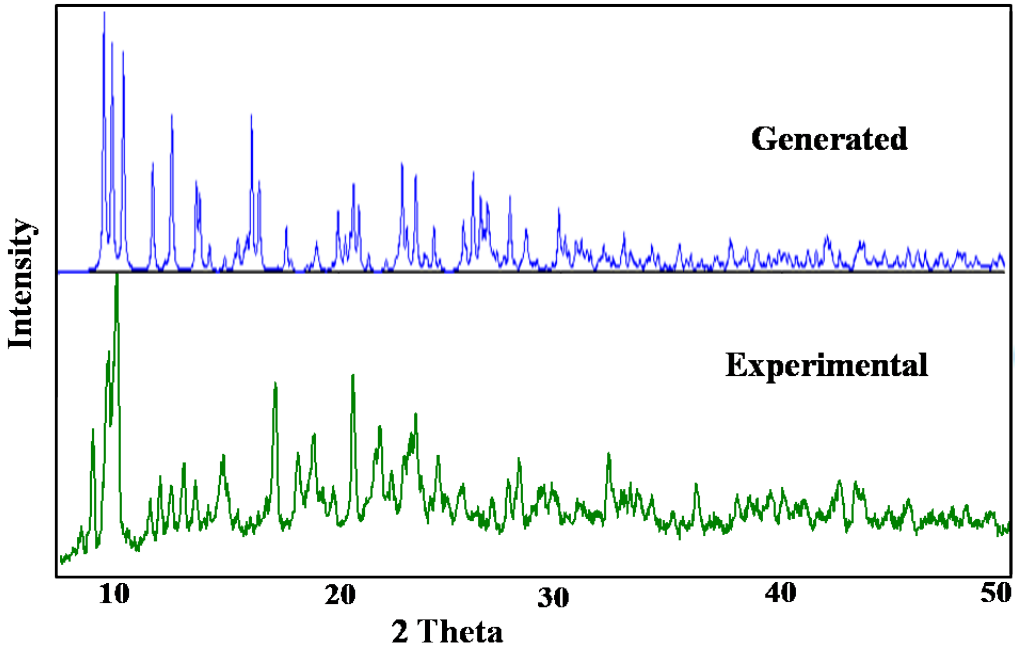
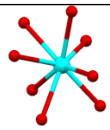
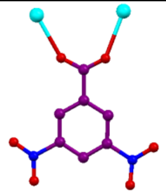
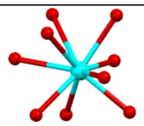
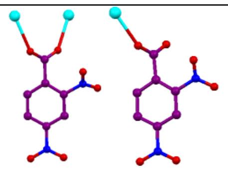


Fig. S8. Showing generated and experimental PXRD patterns of compound (**2**)

Table S7. Coordination numbers of Nd^{III} ion, coordination modes of ligand, Point symbol and topology, dimensionality, M···M distances and chirality of compounds **1** and **2**.

Compound	**Coordination no. of Nd^{III} ion**	**Coordination mode of ligand**	**Point Symbol and topology**	**Loss of solvents, Decomposition temperature (D)**	**M···M distance (Å)**	**Chirality**
1			[1 0 0] chains with 2-c uninodal net	109 °C - loss of one lattice acetonitrile solvent, 320 °C-loss of coordinated water, 414 °C-D	4.267, 5.348	-
2			$\{3^3.4^2.5\}$, [0 1 0] chains, 4-c uninodal SP1-periodic net	68 °C - loss of two coordinated water, 215 °C-loss of acetate anion, 244 °C-D	4.221	Chiral

7. Magnetic study

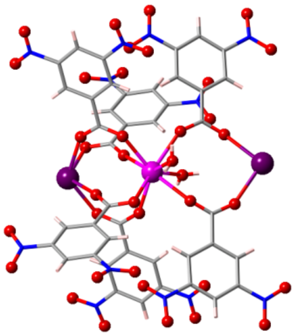
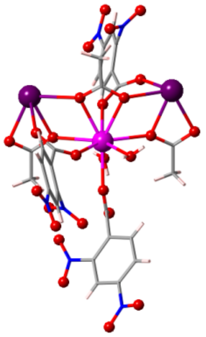
	
1	**2**

Fig. S9. Truncated models for **1** and **2**. Color code: Nd, magenta; La, purple; O, red; N, blue; H, white.

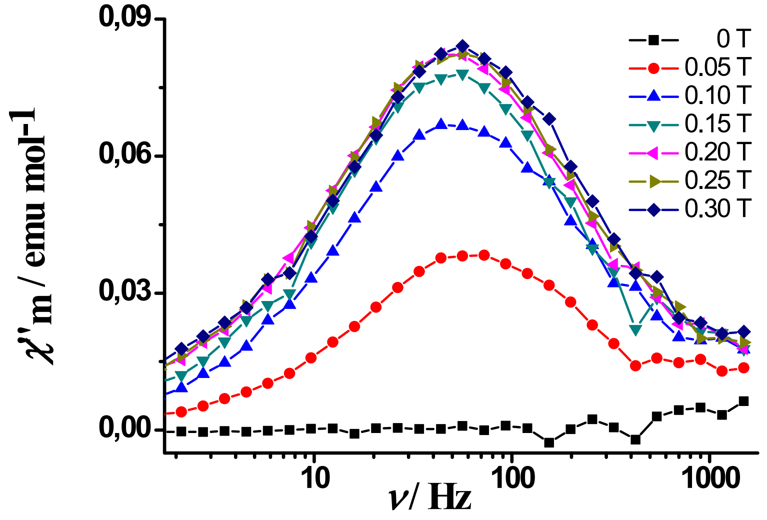


Fig. S10. Frequency dependence of the out-of-phase molar susceptibility (χ_M'') signal at 2 K with applied fields in the 0-0.3 T range for compound **1**.

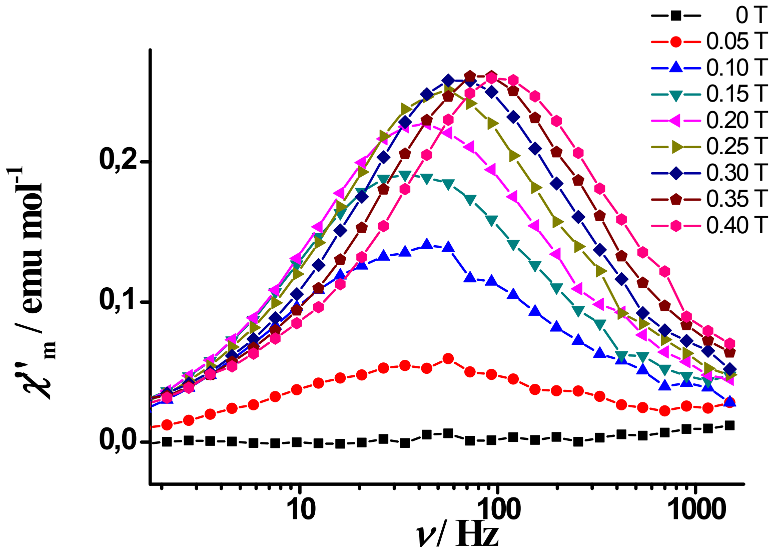


Fig. S11. Frequency dependence of the out-of-phase molar susceptibility (χ_{M}'') signal at 2 K with applied fields in the 0-0.4 T range for compound **2**.

List of frequencies used in the study of the ac frequency-dependence of compounds (**1**) and (**2**) in Fig. 3 (Manuscript):

1488.095, 1284.247, 1102.941, 946.9657, 822.3684, 704.8872, 608.7662, 523.743, 450.7212, 389.0042, 334.8214, 288.4615, 248.6737, 214.0411, 184.5472, 159.1681, 137.0614, 118.0731, 101.6811, 87.61682, 75.48309, 65.01387, 56.00359, 48.25013, 41.57428, 35.80978, 30.85912, 26.58066, 22.89936, 19.72853, 17.00834, 14.64844, 12.61437, 10.87083, 9.36002, 8.06521, 6.95062, 5.98506, 5.1579, 4.44229, 3.82715, 3.29734, 2.84091, 2.44753, 2.10845, 1.81658, 1.5648, 1.34884, 1.16073, 1.00058 Hz.