Supplementary Information

Lanthanide based Coordination Polymers Chill, Relax under Magnetic field and also Fluoresce

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Experimental Section:

Materials: All the reagents and solvents used were commercially available. $Gd(NO_3)_3.xH_2O$, $NdCl_3.xH_2O$, $DyCl_3.xH_2O$ and disodium croconate were obtained from the Alfa Aesar (A Johnson Matthey Company) and were used as supplied without further purification.

Syntheses of the complexes 1, 2 and 3: Complexes **1**, **2** and **3** were synthesized by mixing $Gd(NO_3)_3.xH_2O$, $NdCl_3.xH_2O$ and $DyCl_3.xH_2O$ (0.10 mmol each) respectively with disodium croconate (0.15 mmol, 28 mg) in water and stirring at room temperature for 4-5 hours. These were filtered and the consequent filtrates were kept for slow evaporation. Yellow coloured single crystals suitable for X-ray diffraction were harvested within 2-3 days.

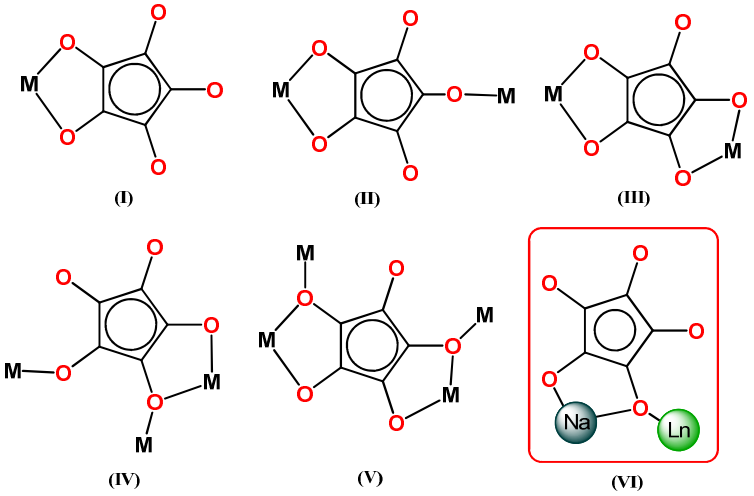
Experimental characterization. Elemental ananlysis calcd (%) for $[GdNa(C_5O_5)_2(H_2O)_7]_n$: C 20.37, H 1.71; found C 20.75, H 1.12; For $[NdNa(C_5O_5)_2(H_2O)_7]_n$: C 20.94, H 2.46; found C 21.05, H 2.20; For $[DyNa(C_5O_5)_2(H_2O)_7]_n$; C 20.30, H 2.38; found C 20.78, H 2.19. Selected FTIR data (ν, KBr pellet, cm^{-1}) :For complex **1**: 3412.(s), 1708 (s), 1638 (s), 1533 (s), 1400 (m), 1115 (w),625 (m); For complex **2**: 3434 (s), 1707 (s), 1636(s), 1522 (s), 1400 (m), 1110 (w), 618(m); For complex **3**: 3413 (s), 1710 (s), 1640 (s), 1528 (s), 1399 (m), 1114 (m), 628 (w).

Physical Measurements: The elemental analyses were carried out on an Elementar Micro vario Cube Elemental Analyzer. FT-IR spectra (4000–400 cm^{-1}) were recorded on KBr pellets with a Perkin Elmer Spectrum BX spectrometer. Powder X-ray diffraction (PXRD) data were collected on a PANalytical EMPYREAN instrument using Cu-*K*α radiation. All the solid state fluorescence measurements were recorded on a HORIBA JOBINYVON FLUOROLOG3-111. Complexes **1-3** were excited at 280 nm and the emission spectra were recorded between 300 nm to 500 nm. The excitation and emission slits were kept at 2 and 3 nm.

X-ray Single-Crystal Structure Determination: X-ray crystallographic data were collected at 120 K on a Brüker Smart Apex II CCD diffractometer using graphite monochromated MoKα (λ = 0.71073 Å) radiation. Data collection was performed using φ and ω scan. The structures were solved using direct methods followed by full matrix least square refinements against F^2 (all data HKLF 4 format) using SHELXTL. Anisotropic refinement was used for all non-hydrogen atoms. Organic hydrogen atoms were placed in appropriate calculated positions.

Magnetic measurements: Magnetic measurements were performed using a Quantum Design VSM SQUID magnetometer. The measured values were corrected for the experimentally measured contribution of the sample

holder, while the derived susceptibilities were corrected for the diamagnetism of the samples, estimated from Pascal's tables (Ref. O. Kahn, *Molecular Magnetism*; Wiley-VCH: New York, 1993).



Scheme S1 Left- Different coordination modes of the organic ligand (disodium croconate) used. Right- Specific binding mode for the complexes **1- 3**.

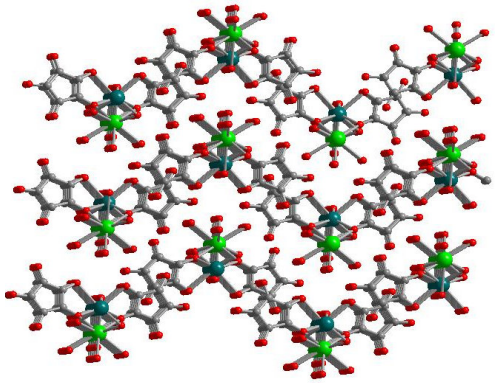


Fig. S1 Packing diagram of complex 1. Colour code: lime green Ln; gray C; red O; greenish blue Na.

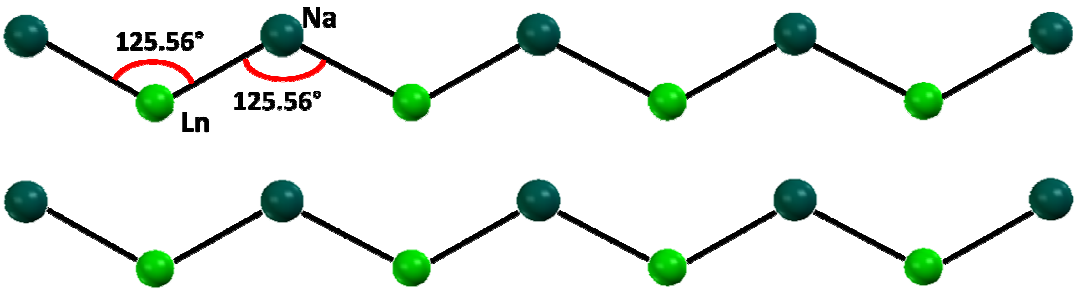


Fig. S2 Illustration of **1D** zigzag chain formed by the alternate arrangement of the Ln^{3+} and Na^{+} atoms found in complex **1**.

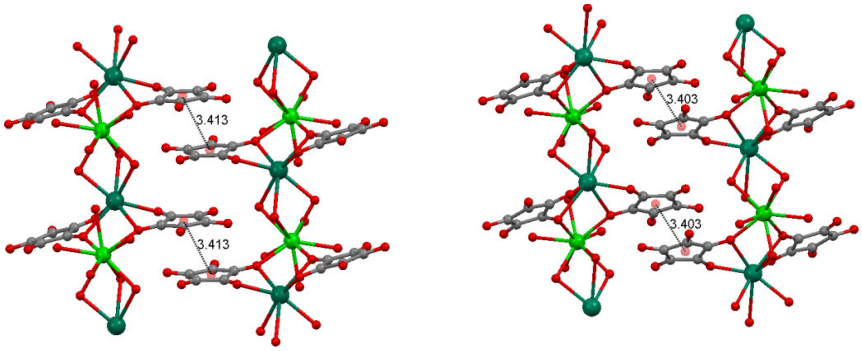


Fig. S3 Illustration of π-π stacking interactions observed in the complexes **2** (left) and **3** (right) interconnecting the 1D chain (Unit in Å). Colour code: same as in Fig. S2.

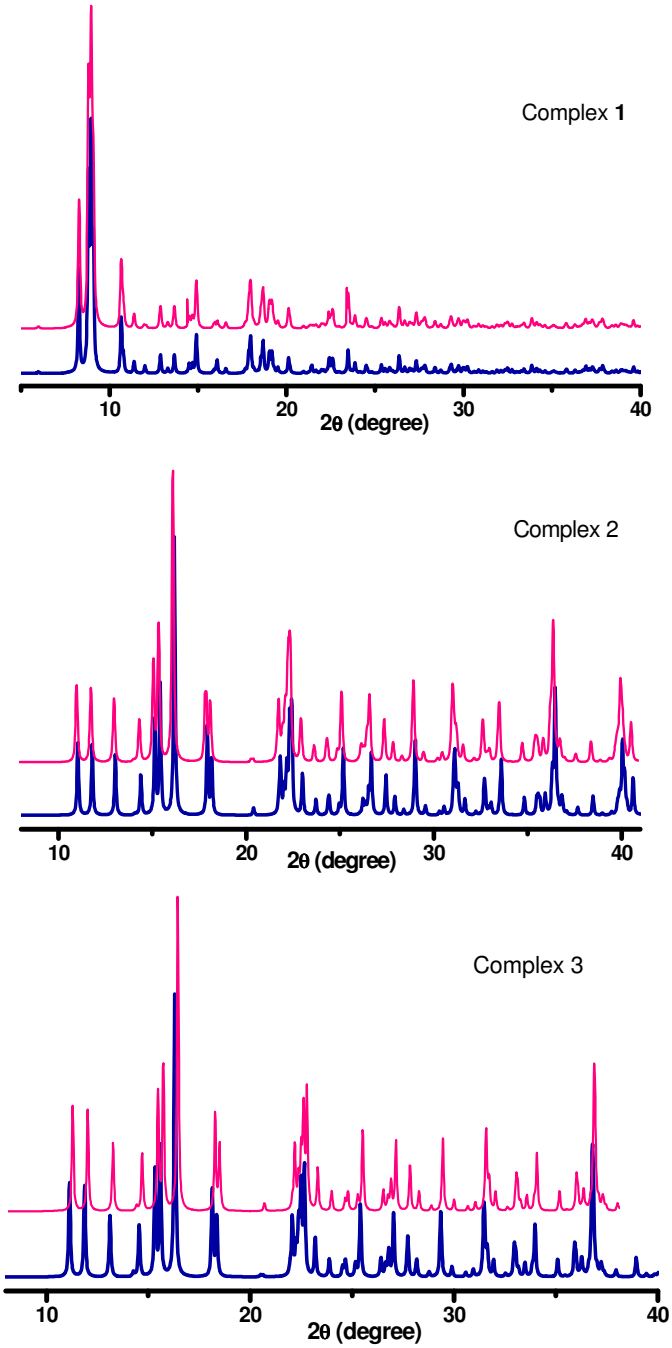


Fig. S4 Experimental (pink) and simulated (blue) powder XRD data for complexes **1** (a), **2** (b), and **3** (c).

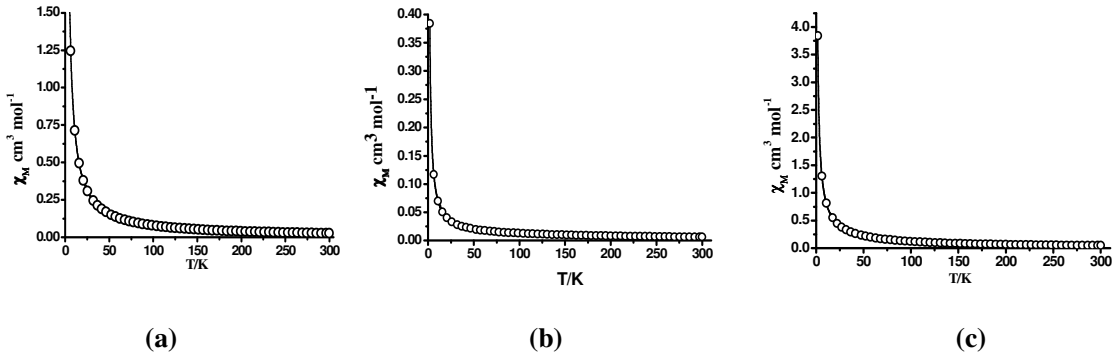


Fig. S5 Temperature dependence of χ_M for complexes **1**(a), **2**(b) and **3**(c) measured at 2-300 K.

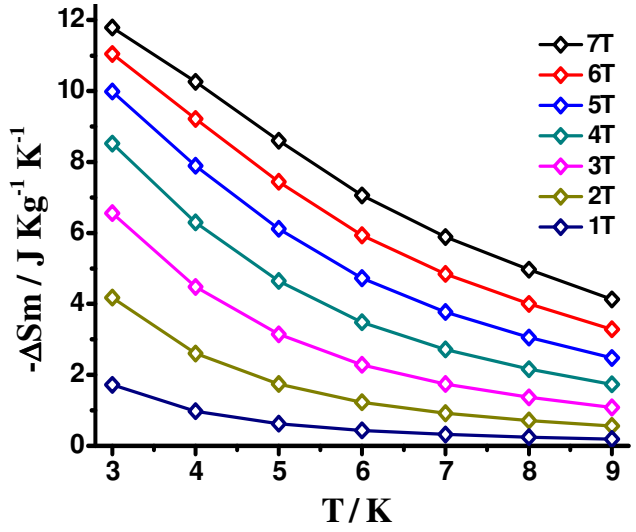


Fig. S6 Temperature dependencies of $-\Delta S_m$ as obtained from magnetization data for complex **2**.

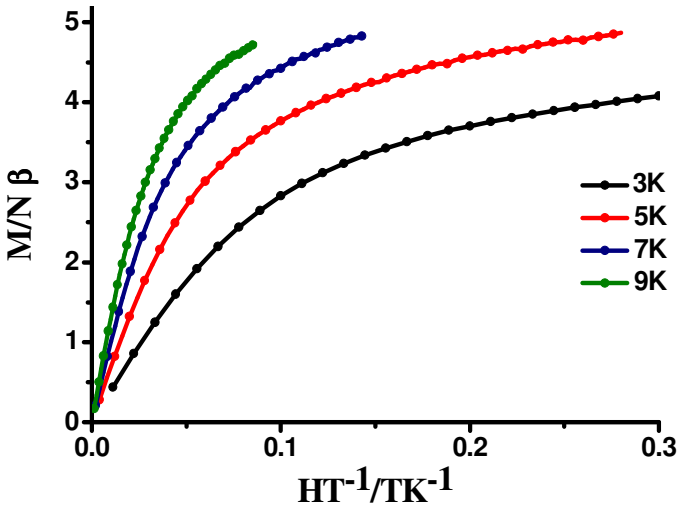
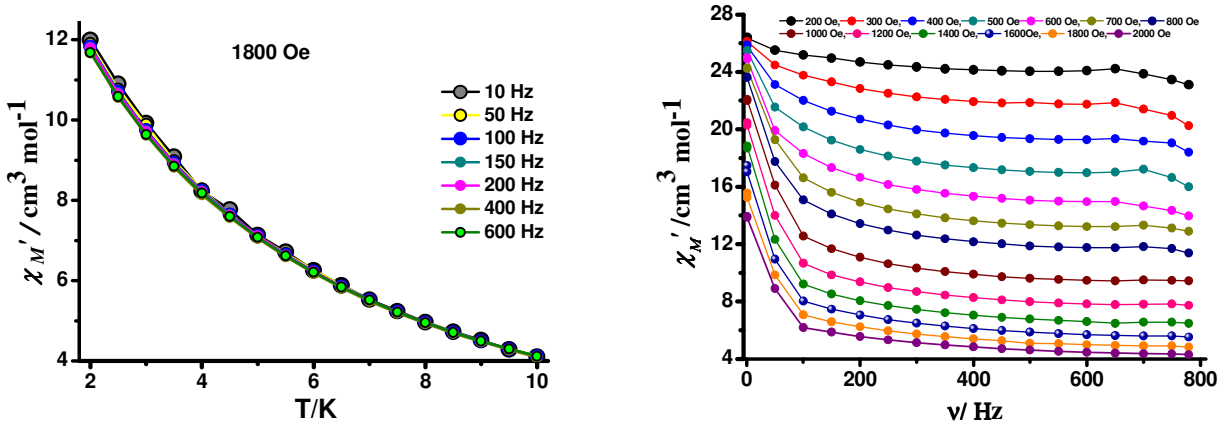
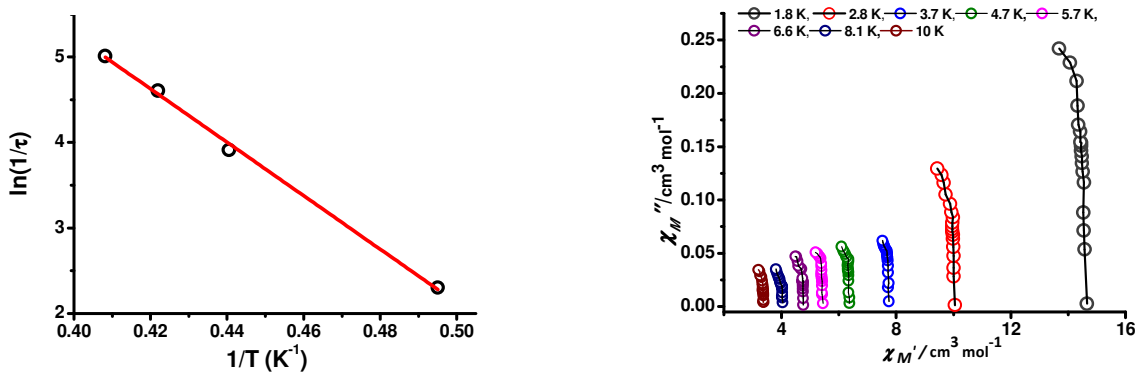


Fig. S7 M/Nβ *vs* H/T plots for complex **3** measured at 3-9 K.



(a) (b)

Fig. S8 (a) Temperature dependence of χ_M' for complex **3**, measured in 3.5 G ac field and 1800 Oe dc field. (b) Frequency dependence of χ_M' for complex **3**.



(a) (b)

Fig. S9 (a) Plot of relaxation time *vs*. reciprocal temperature for **3** under zero-*dc* field. The red solid line is fitted with the Arrhenius law. (b) Cole–Cole plots measured at 1.8-10 K under zero dc field.

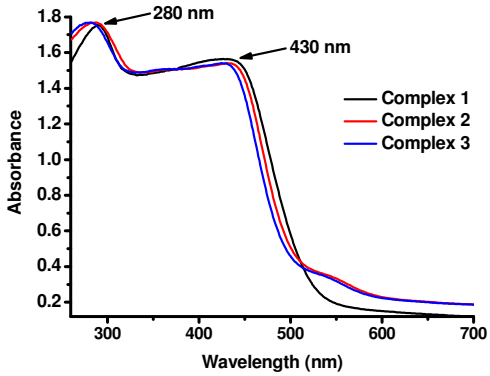


Fig. S10 UV-visible spectra of the complexes in solid state at room temperature.

Table S1. Bond distances (Å) and bond angles (°) around Ln^{3+} and Na^{+} centres found in complexes **1 - 3**.

1		**2**		**3**	
Gd1 – O1	2.385(2)	Nd1 – O1	2.432(3)	Dy1 – O1	2.346(2
Gd1 – O6	2.458(2)	Nd1 – O6	2.618(5)	Dy1 – O6	2.414(3)
Gd1 – O7	2.410(2)	Nd1 – O7	2.541(4)	Dy1 – O7	2.415(2)
Gd1 – O8	2.466(2)	Nd1 – O8	2.487(3)	Dy1 – O8	2.387(2)
Gd1 – O9	2.601(3)	Nd1 – O9	2.461(3)	Dy1 – O9	2.444(2)
Gd1 – O10	2.420(3)	Nd1 – O10	2.474(7)	Dy1 – O10	2.573(3)
Gd1 – O1A	2.385(2)	Nd1 – O1A	2.432(3)	-	-
Gd1 – O6A	2.458(2)	Nd1 – O7A	2.541(4)	-	-
Gd1 – O8A	2.466(2)	Nd1 – O8A	2.487(3)	-	-
Na1 – O1	2.558(2)	Na1 – O1	2.591(4)	Dy1 – O1	2.560(2)
Na1 – O2	2.476(2)	Na1 – O5	2.462(4)	Dy1 – O2	2.441(3)
Na1 – O8	2.442(2)	Na1 – O6	2.846(5)	Dy1 – O6	3.049(2)
Na1 – O9	2.857(3)	Na1 – O7	2.486(5)	Dy1 – O9	2.460(2)
Na1 – O8A	2.442(2)			Dy1 – O10	2.826(3)
O1 − Gd1 – O6	70.73(6)	O1 − Gd1 – O6	72.3(1)	O1 − Dy1 – O6	69.80(8)
O1 − Gd1 – O7	138.82(7)	O1 − Gd1 – O7	136.7(1)	O1 − Dy1 – O7	136.51(6)
O1 − Gd1 – O8	136.25(5)	O1 − Gd1 – O8	70.5(1)	O1 − Dy1 – O8	139.33(8)
O1 − Gd1 – O9	71.83(7)	O1 − Gd1 – O9	138.5(1)	O1 − Dy1 – O9	136.08(6)
O1 − Gd1 – O10	69.46(8)	O1 − Gd1 – O10	69.2(2)	O1 − Dy1 – O10	71.33(8)
O1 − Gd1 – O1A	79.46(6)	O1 − Gd1 – O1A	79.8(1)	O1 − Dy1 – O1A	78.92(6)
O1− Gd1 – O6A	136.19(6)	O1− Nd1 – O7A	86.0(1)	O1− Dy1 – O7A	71.76(6)
O1 − Gd1 – O8A	85.68(5)	O1 − Gd1 – O8A	136.3(1)	O1 − Dy1 – O9A	85.27(6)
O6− Gd1 – O1A	136.19(6)	-	-	-	-
O6 − Gd1 – O7	69.29(7)	O6 − Gd1 – O7	64.4(1)	O6 − Dy1 – O7	70.27(8)
O6 − Gd1 – O8	137.81(5)	O6 − Gd1 – O8	124.5(1)	O6 − Dy1 – O8	105.78(9)
O6 − Gd1 – O9	124.61(7)	O6 − Gd1 – O9	125.8(1)	O6 − Dy1 – O9	140.50(7)
O6 − Gd1 – O10	70.36(8)	O6 − Gd1 – O10	129.1(2)	O6 − Dy1 – O10	128.94(9)
O6 − Gd1 – O6A	110.69(5)	O7 − Gd1 – O7A	76.8(1)	O7 − Dy1 – O7A	109.58(6)
O6 − Gd1 – O8A	73.40(5)	O7 − Gd1 – O8A	73.2(1)	O7 − Dy1 – O8	69.02(8)
O7 − Gd1 – O8	73.95(7)	O7 − Gd1 – O8	137.3(1)	O7 − Dy1 – O9	137.81(6)
O7 − Gd1 – O9	125.78(8)	O7 − Gd1 – O9	73.9(1)	O7 − Dy1 – O9A	73.08(6)
O7 − Gd1 – O10	105.30(9)	O7 − Gd1 – O10	141.2(1)	O7 − Dy1 – O10	125.15(8)
O8 − Gd1 – O8A	77.21(5)	O8 − Gd1 – O8A	110.8(1)	O8 − Dy1 – O9	73.56(8)
O8 − Gd1 – O9	64.45(7)	O8 − Gd1 – O9	69.0(1)	O8 − Gd1 – O10	125.3(1)
O8 − Gd1 – O10	141.07(8)	O8 − Gd1 – O10	70.6(2)	O9 − Gd1 – O9A	78.33(6)
O9 − Gd1 – O10	128.93(9)	O9 − Gd1 – O10	105.0(2)	O9 − Gd1 – O10	64.80(8)
O1 − Na1 – O1A	73.16(6)	O1 − Na1 – O1A	74.1(1)	O1 − Na1 – O1A	71.22(7)
O1 − Na1 – O2	69.07(6)	O1 − Na1 – O5	120.7(2)	O1 − Na1 – O2	69.51(8)
O1 − Na1 – O2A	119.12(7)	O1 − Na1 – O5A	69.0(1)	O1 − Na1 – O2A	118.80(9)
O1 − Na1 – O8	138.86(7)	O1 − Na1 – O6	142.7(2)	O1 − Na1 – O6	57.31(7)
O1 − Na1 – O8A	90.12(7)	O1 − Na1 – O7	87.3(1)	O1 − Na1 – O9	90.42(7)
O1 − Na1 – O9	143.39(8)	O1 − Na1 – O7A	135.9(2)	O1 − Na1 – O9A	137.55(8)
O1 − Na1 – O10	57.94(7)	O5 − Na1 – O5A	92.3(2)	O1 − Na1 – O10	144.29(9)
O2 − Na1 – O2A	90.14(7)	O5 − Na1 – O6	88.0(2)	O2 − Na1 – O2A	91.16(9)
O2 − Na1 – O8	147.33(8)	O5 − Na1 – O7	87.0(1)	O2 − Na1 – O6	124.99(9)
O2 − Na1 – O8A	87.11(7)	O5 − Na1 – O7A	149.6(2)	O2 − Na1 – O9	148.06(9)
O2 − Na1 – O9	86.58(7)	O6 − Na1 – O7	61.7(1)	O2 − Na1 – O9A	87.28(8)
O2 − Na1 – O10	125.43(8)	O7 − Na1 – O7A	78.8(1)	O2 − Na1 – O10	87.36(9)
O8 − Na1 – O8A	78.12(6)	Nd1 − O1 – Na1	101.2(1)	O6 − Na1 – O9	80.44(7)
O8 − Na1 – O9	60.77(7)	Nd1 – O6 – Na1	89.8(2)	O6 − Na1 – O10	128.76(9)
O8 − Na1 – O10	81.20(8)	Nd1 – O7 – Na1	100.3(1)	O9 − Na1 – O9A	77.71(7)
O9 − Na1 – O10	129.67(9)	-	-	O9 − Na1 – O10	60.71(8)
Gd1 − O1 – Na1	101.50(7)	-	-	Dy1 − O1 – Na1	102.67(7)
Gd1 – O8 – Na1	101.07(6)	-	-	Dy1 – O6 – Na1	88.33(8)
Gd1 – O9 – Na1	87.79(8)	-	-	Gd1 – O9 – Na1	100.57(7)
Gd1 − O10 – Na1	88.54(9)	-	-	Gd1 − O10 – Na1	88.51(9)

Table S2. Hydrogen bonding distances (Å) and angles (deg) for the complex **1** $[GdNa(C_5O_5)_2(H_2O)_7]_n$ (D: donor, A: acceptor).

D-H….A	Symmetry operation	D-H (Å)	D....A (Å)	H….A (Å)	<D-H-A (deg)
O6-H6...O5	x,y,z	0.820	2.768(2)	2.472	102.48
O6-H6...O2	x+1,+y,+z+1	0.820	2.758(2)	1.944	172.14
O7-H7...O2	x+1,-y+1/2,+z+1	0.820	2.985(3)	2.416	127.25
O10-H10...O4	-x+1,+y+1/2,-z+1	0.820	2.820(3)	2.063	153.40
O4...O7	-x,-y,-z+1	-	2.910(3)	-	-
O5...O8	-x,+y-1/2,-z+1	-	2.734(2)	-	-
O4...O9	- x+1,+y-1/2,-z+2	-	2.819(2)	-	-
O3...O8	-x+1,+y-1/2,-z+2	-	2.692(2)	-	-

Table S3. Hydrogen bonding distances (Å) and angles (deg) for the complex **2** $[NdNa(C_5O_5)_2(H_2O)_7]_n$ (D: donor, A: acceptor).

D-H….A	Symmetry operation	D-H(Å)	D....A(Å)	H….A(Å)	<D-H-A(deg)
O8-H8...O2	x,-y+1/2,+z	0.820	2.815(4)	2.001	171.48
O9-H9...O5	x+1,-y+1/2,+z+1	0.820	2.944(4)	2.827	90.11
O10-H10...O3	-x,+y+1/2,-z+2	0.820	2.821(6)	2.053	155.76
O9...O3	-x+1,-y,-z+2	-	2.941(5)	-	-
O5...O8	x+1,-y+1/2,+z+1	-	2.752(4)	-	-
O3...O6	-x,-y,-z+1	-	2.836(4)	-	-
O4...O7	-x,+y+1/2,-z+1	-	2.685(4)	-	-
O7...O2	-x+1,+y+1/2,-z+2	-	2.722(4)	-	-

Table S4. Hydrogen bonding distances (Å) and angles (deg) for the complex **3** $[DyNa(C_5O_5)_2(H_2O)_7]_n$ (D: donor, A: acceptor).

D-H….A	Symmetry operation	D-H(Å)	D....A(Å)	H….A(Å)	<D-H-A(deg)
O7-H7...O5	x,y,z	0.820	2.791(2)	2.475	103.37
O6-H6...O4	-x,-y,-z	0.820	2.826(3)	2.224	140.24
O8-H8...O4	x,-y+1/2,+z	0.820	2.900(3)	2.537	107.73
O7...O2	x,-y+1/2,+z	-	2.754(2)	-	-
O2...O3	-x+2,-y,-z+1	-	3.026(3)	-	-
O2...O8	x+1,+y,+z+1	-	3.014(4)	-	-
O3...O9	-x+1,+y-1/2,-z+1	-	2.675(2)	-	-
O4...O10	-x+1,-y,-z+1	-	2.842(3)	-	-
O5...O9	-x,+y-1/2,-z	-	2.702(2)	-	-