Supporting Information

Synthesis, structure and magnetic properties of Nd^{3+} and Pr^{3+} 2D polymers with tetrafluoro-*p*-phthalate

Elena A. Mikhalyova,[a] *Sergey V. Kolotilov,*[a] *Matthias Zeller,*[b] *Laurence K. Thompson,*[c]
*Anthony W. Addison**[d], *Vitaly V. Pavlishchuk**[a] *and Allen D. Hunter*[b]

[a] L. V. Pisarzhevskii Institute of Physical Chemistry of the National Academy of Sciences of the Ukraine, Prospekt Nauki 31, Kiev, 03028 Ukraine, tel. (38 044) 525 42 28, fax (38 044) 525 62 16;

[b] STaRBURSTT CyberInstrumentation Consortium and Department of Chemistry, Youngstown State University, One University Plaza, Youngstown OH 44555-3663, U.S.A.;

[c] Department of Chemistry, Memorial University, St. John’s, NL, Canada A1B 3X7

[d] Department of Chemistry, Drexel University, Philadelphia, PA 19104-2816, U.S.A.

Table S1. Crystallographic and structure refinements data for complex **1**

Empirical formula	$C_{18}H_{14}N_2O_8PrF_6$
Moiety formula	$C_{18}H_{14}F_6N_2O_8Pr$, 1.684(C_3H_7NO)
F.W.	641.22
Crystal size (mm)	0.38 × 0.35 × 0.1
Space group	C2
a (Å)	22.194(2)
b (Å)	11.4347(12)
c (Å)	11.7160(12)
β (deg)	94.703(2)
V (Å^3)	2963.3(5)
d_{calc}, (g·cm^{-3})	1.713
Z	4
T (K)	100(2)
λ (Å)	0.71073
μ (mm^{-1})	1.738
θ range for data collection:	1.74 to 28.28° (99.7% complete)
Reflections collected	14033
Reflections unique	7263 (R(int) = 0.0155)
Parameter / Restraints	395 / 239
Goodness-of-fit on F^2:	1.133
R_1 [$I>2\sigma(I)$]^a	0.0344
wR_2 [$I>2\sigma(I)$]^b	0.0935
Absolute structure factor	0.46(2)
Largest diff. peak and hole:	1.537 and -0.683 e × Å^{-3}

[a] $R_1 = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$, [b] $wR_2 = \{\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]\}^{1/2}$

Description of Disorder and Pseudosymmetry.

The structure of compound 1 exhibits both coordinated and solvate DMF molecules, all of which are disordered. The solvate DMF molecules were refined isotropically, all other non hydrogen atoms were refined anisotropically.

The non-disordered part of the structure exhibits a pseudo-center of inversion resembling the space group C2/m. However, this pseudo symmetry is not absolutely exact and attempts to refine the structure in C2/m required to refine the tetrafluoro terephthalte ligands as disordered over two positions. The higher symmetry is also not present for the disordered DMF molecules. Thus the structure was refined as an inversion twin in the better fitting space group C2; the BASF factor refined to 0.46(2).

The DMF molecules show disorder and partially a large degree of thermal motion. One DMF molecule is located in a void with no close contact with the other molecules of the structure. This molecule is disordered over two positions by a pseudo mirror plane. The occupancy ratio refined to 0.56(2) to 0.44(2). The disorders of the other DMF molecules (two coordinated to the metal center and one not coordinated) are dependent on each other. The two coordinated DMF molecules are disordered over two positions each with a shared occupancy ratio of 0.684(6) to 0.316(6). For the major 68.4% orientation this leaves a void between the two coordinated DMF molecules. This void is filled with the last uncoordinated DMF molecule. For the minor 31.6% orientation no void large enough for another DMF molecule is present.

All DMF molecules were restrained to have the same geometries and to be flat, and some of the equivalent atoms were restrained to have identical anisotropic displacement parameters (C17 and C17b, C16 and C16b, N1 and N1b, C18 and C18b, C19 and C19b, C20 and C20b, N2 and N2b, C15 and C15b) and/or to be isotropic within a standard deviation of 0.03 Å2 (N1, C16, C17, C18, C19, N2, and C20)

All hydrogen atoms were placed geometrically and were refined with an isotropic displacement parameter 1.5 (methyl) or 1.2 times (all others) that of the neighboring carbon atom.

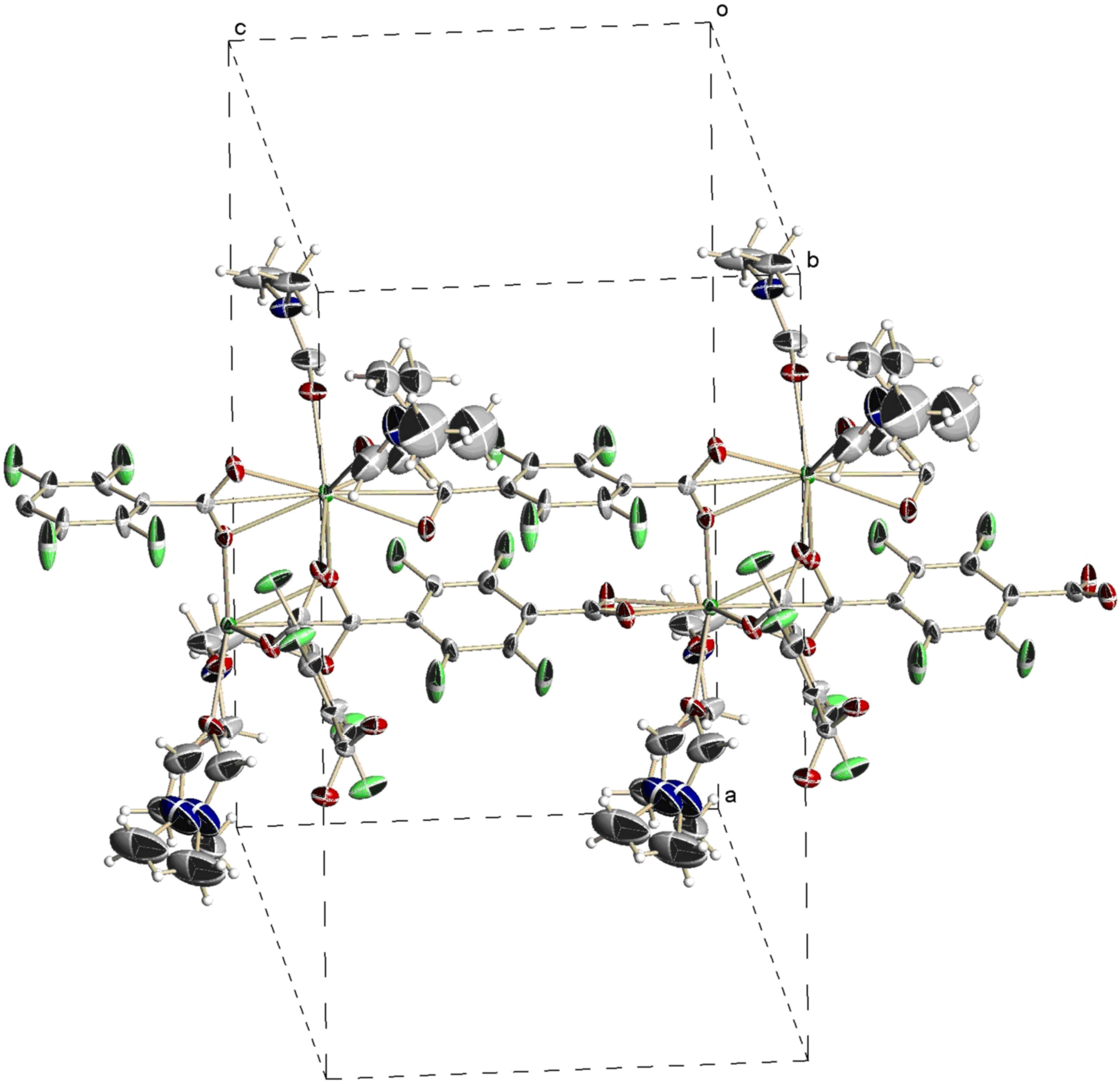


Figure S1. Partial packing view of the structure of **1** with 50% thermal ellipsoids. Non-coordinated solvate DMF molecules are omitted for clarity.

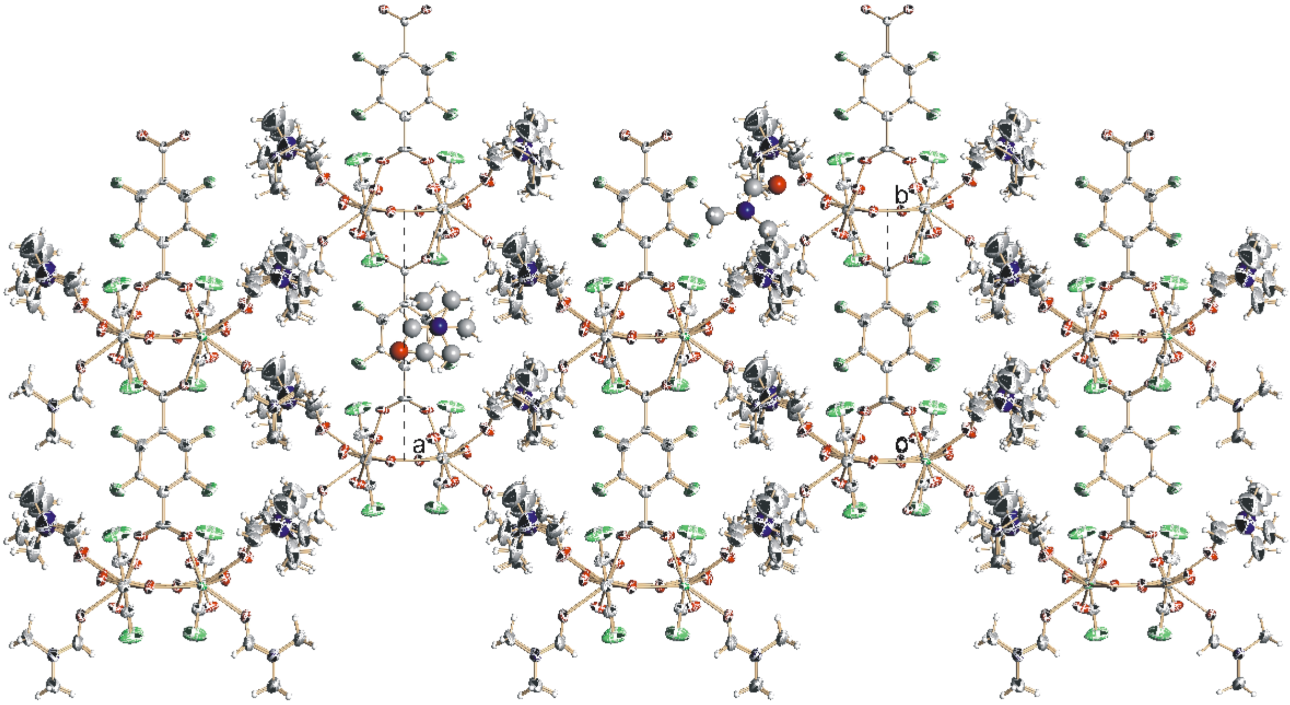


Figure S2. Complete packing view of the structure of **1** with 50% thermal ellipsoids. Atoms refined isotropically are represented as spheres of arbitrary radius. The view is down the *a*-axis showing the twofold axis along *b* and the pseudo-mirror plane through *b*.

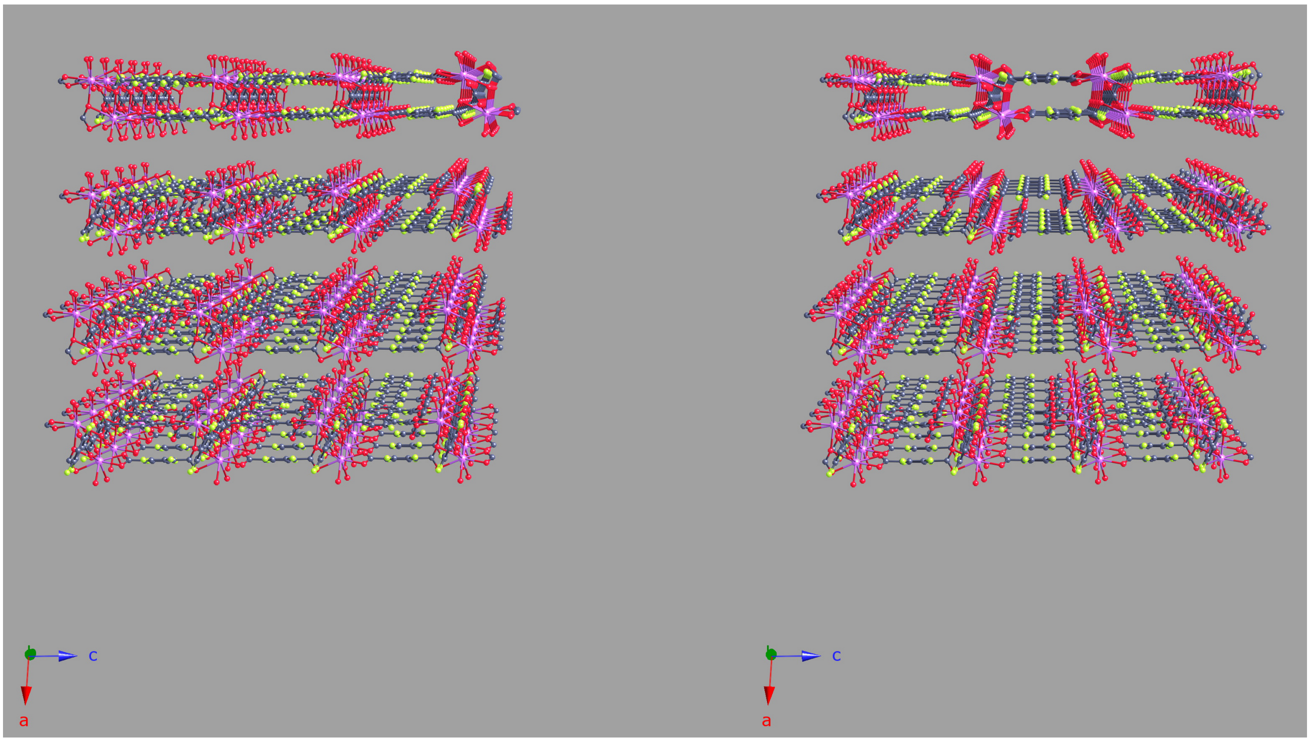


Figure S3. Inverse stereoview of compound-1 lattice, viewed along the b-axis, with DMF molecules removed.

Table S2. Selected interatomic distances for **1**

Selected distances (Å)	
Pr(1)-Pr(1)'	4.181(4)
Pr(1)-O(1)	2.656(2)
Pr(1)-O(1)'	2.470(3)
Pr(1)-O(2)	2.583(3)
Pr(1)-O(3)	2.546(4)
Pr(1)-O(4)	2.536(3)
Pr(1)-O(5)	2.436(5)
Pr(1)-O(6)	2.457(5)
Pr(1)-O(8)	2.442(3)
Pr(1)-O(9)	2.468(4)

Table S3. Selected angles for **1**

Selected angles (deg)	
O(5)–Pr(1)–O(8)	141.53(16)
O(5)–Pr(1)–O(6)	133.36(9)
O(8)–Pr(1)–O(6)	73.86(14)
O(5)–Pr(1)–O(9)	77.80(17)
O(8)–Pr(1)–O(9)	72.57(14)
O(6)–Pr(1)–O(9)	146.30(16)
O(5)–Pr(1)–O(1)	74.2(2)
O(8)–Pr(1)–O(1)	142.69(18)

O(6)–Pr(1)–O(1)	70.32(19)
O(9)–Pr(1)–O(1)	141.53(19)
O(5)–Pr(1)–O(4)	127.62(14)
O(8)–Pr(1)–O(4)	74.28(14)
O(6)–Pr(1)–O(4)	82.55(17)
O(9)–Pr(1)–O(4)	85.68(16)
O(1)–Pr(1)–O(4)	90.93(14)
O(5)–Pr(1)–O(3)	76.56(15)
O(8)–Pr(1)–O(3)	117.20(14)
O(6)–Pr(1)–O(3)	119.40(16)
O(9)–Pr(1)–O(3)	74.67(15)
O(1)–Pr(1)–O(3)	73.56(13)
O(4)–Pr(1)–O(3)	51.10(11)
O(5)–Pr(1)–O(2)	78.59(15)
O(8)–Pr(1)–O(2)	72.31(13)
O(6)–Pr(1)–O(2)	93.36(15)
O(9)–Pr(1)–O(2)	79.30(13)
O(1)–Pr(1)–O(2)	119.42(10)
O(4)–Pr(1)–O(2)	146.13(13)
O(3)–Pr(1)–O(2)	147.11(12)
O(5)–Pr(1)–O(1)	71.86(19)
O(8)–Pr(1)–O(1)	105.43(15)
O(6)–Pr(1)–O(1)	68.5(2)
O(9)–Pr(1)–O(1)	124.01(15)
O(1)–Pr(1)–O(1)	70.66(9)
O(4)–Pr(1)–O(1)	149.41(17)
O(3)–Pr(1)–O(1)	137.25(14)
O(2)–Pr(1)–O(1)	49.56(9)
Pr(1)-O(1)-Pr(1)'	109.26(9)

Pr(1)-O(5)-Pr(1)'	78.82(7)
Pr(1)-O(6)-Pr(1)'	78.60(7)

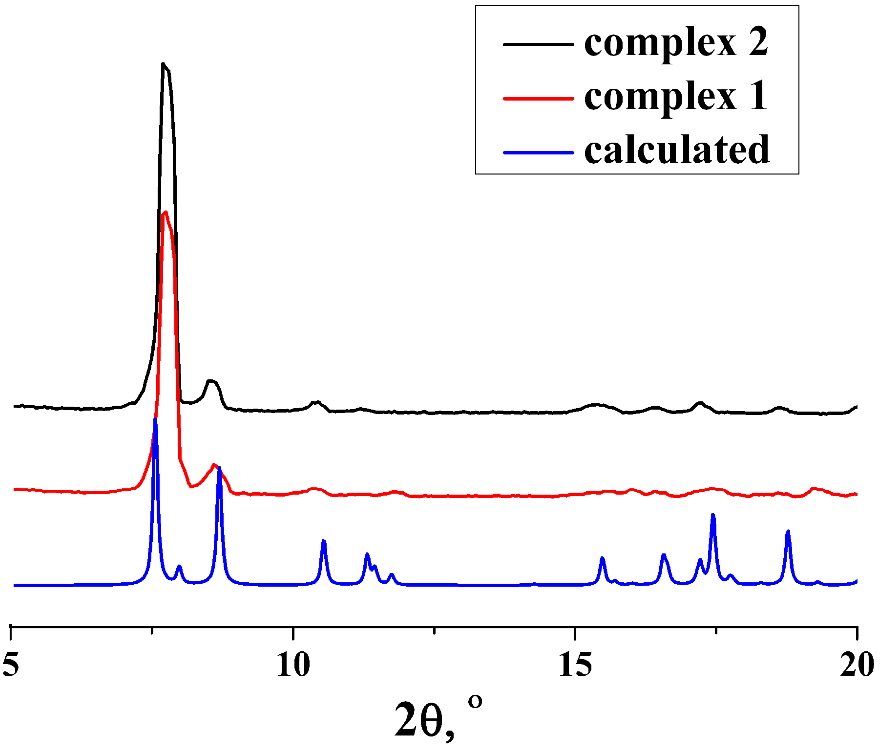


Figure S4. X-ray powder diffraction patterns for air-dried samples of complexes **1** and **2**, along with that calculated from the X-ray structures (λ = 1.5406 Å).

Table S4. Structural features of $Ln_2(\mu\text{-}O)_2(\mu\text{-}OCO)_2$ dinuclear units and 2D planes in selected lanthanide (III) *p*-benzenedicarboxylato polymers. ρ is the angle between $Ln_2(\mu\text{-}O)_2$ and $Ln_2(\mu\text{-}OCO)_2$ planes (degrees), δ is the difference between Ln–(μ-O) and Ln'–(μ-O) distances (Å)

Compound [a)]	ρ, °	δ, Å	ω, °	**ref.** [b)]
1	90	0.19(1)	90	this work
$Eu(atp)_{1.5}(phen)(H_2O)$	83.7(5)	0.90(1)	55.6(5)	21
$La(atp)_{1.5}(phen)(H_2O)$	82.4(5)	0.53(1)	55.7(5)	21
$Er_2(atp)_3(phen)_2(H_2O)$	83.1(5)	0.91(1)	56.2(5)	21
$Tb_2(atp)_3(phen)_2(H_2O)$	82.9(5)	0.81(1)	56.1(5)	21
$La_2(ndc)_3(phen)_2(H_2O)_2$	85.3(5)	0.38(1)	83.8(5)	25
$Eu_2(ndc)_3(phen)_2(H_2O)_2$	84.8(5)	0.70(1)	83.1(5)	25
$Ho_2(ndc)_3(phen)_2(H_2O)_2$	85.8(5)	0.91(1)	82.6(5)	25
$Eu(bdc)_{3/2}(phen)(H_2O)$	85.8(5)	1.03(1)	54.2(5)	26
$Yb_2(bdc)_3(phen)_2(H_2O)$	83.8(5)	1.03(1)	56.45(50)	26
$Nd_2(ndc)_3(DMF)_4\cdot H_2O$	88.6(5)	0.24(1)	86.85(50)	27
$La_2(ndc)_3(DMF)_4\cdot H_2O$	88.4(5)	0.23(1)	86.9(5)	27
$Eu_2(ndc)_3(DMF)_4$	89.3(5)	0.28(1)	86.3(5)	27
$La_2(bdc)_3(H_2O)_2(phen)_2$	86.7(5)	0.80(1)	54.4(5)	28
$[Eu(bdc)(MeOH)_4]Cl\cdot MeOH\cdot 0.25H_2O$	88.7(5)	0.59(1)	77.9(5)	29
$[Gd(bdc)(MeOH)_4]Cl\cdot MeOH\cdot 0.25H_2O$	88.2(5)	0.67(1)	76.5(5)	29
$[Tb(bdc)(MeOH)_4]Cl\cdot MeOH\cdot 0.25H_2O$	88.6(5)	0.74(5)	76.9(5)	29
$[Eu(bdc)NO_3(MeOH)_2]\cdot MeCN\cdot H_2O$	87.9(5)	0.40(5)	86.9(5)	29
$[Gd(bdc)NO_3(MeOH)_2]\cdot MeCN\cdot H_2O$	88.0(5)	0.41(5)	86.9(5)	29

[a] atp = 2-aminoterephthalate; phen = 1,10-phenanthroline; nda = 1,4-naphthalenedicarboxylate; bdc = 1,4-benzenedicarboxylate (*p*-phthalate, terephthalate); DMF = dimethylformamide; DEF = diethylformamide; L = tetrafluoroterephtalate.

[b] references are from reference list of the main text

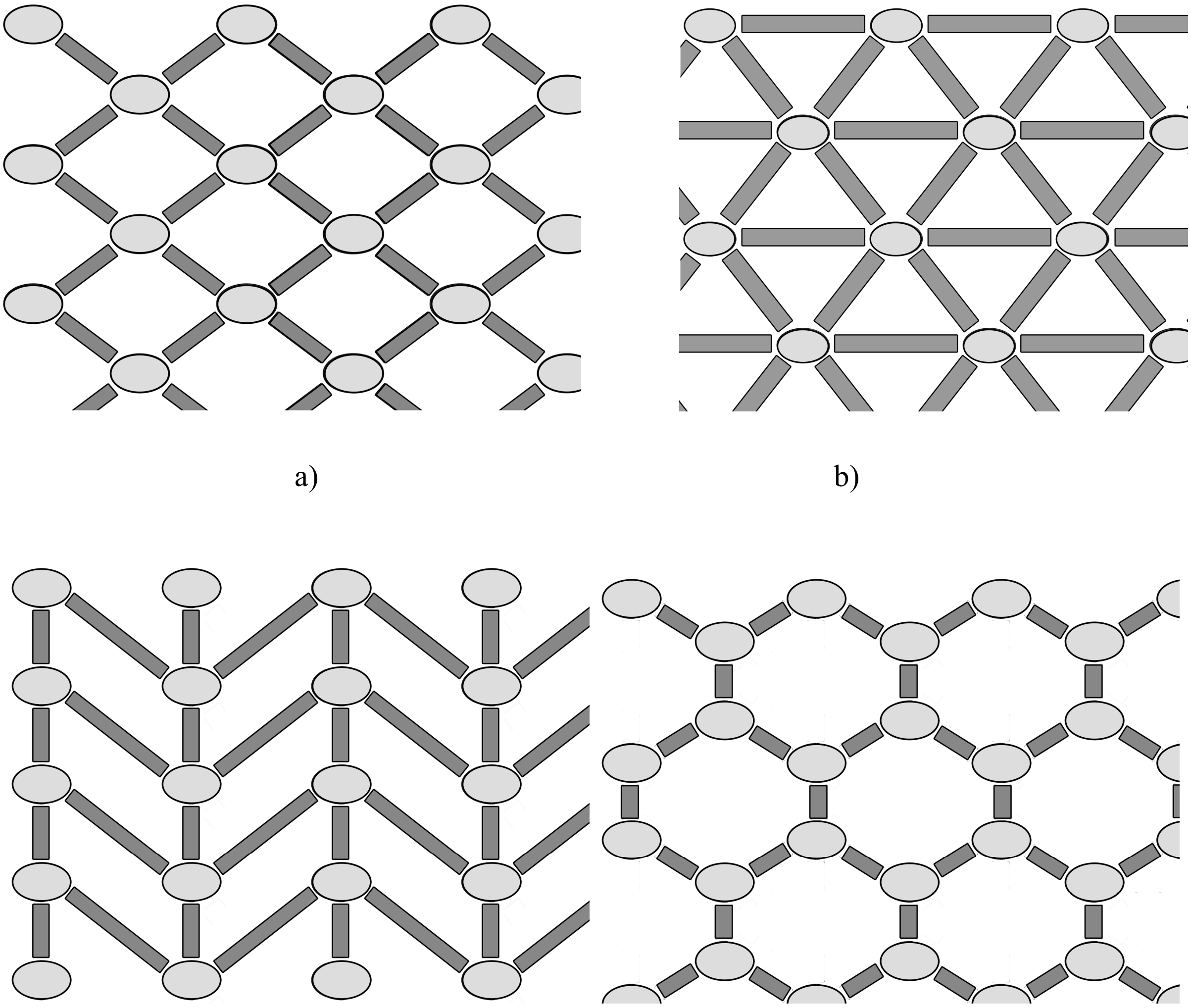
Table S5. Reported coordination polymers of lanthanides (III) with *p*-phthalate and its derivatives and their assignment to structural types according to proposed classification.

Compound [a)]	**Type**	**ref.** [b)]
1	2B2a	this work
$Ln_2(atp)_3(DMF)_4$ (Ln = Pr, Eu, Gd, Tb, Dy)	3B2	5
$Ln(bdc)(DMF)_2(NO_3)$ (Ln = Tb, Eu)	3Ca	11
$Ln_2(btp)_3.2H_2O$ (Ln = La, Pr)	3Ca	13
$Er_2(bdc)_3(H_2O)_6$	2B2a	14
$Er_2(bdc)_3(H_2O)_8\cdot 2H_2O$	1B2	15
$Er_2(bdc)_3(H_2O)_6\cdot 2H_2O$	3Cc	15
$Er_2(bdc)_3(H_2O)_6\cdot H_2O$	3P	15
$Er_2(bdc)_3(H_2O)_6\cdot 2H_2O$	3Cd	15
$Er_4(bdc)_6\cdot 6H_2O$	3P	16
$Gd_2(bdc)_3(DMF)_2(H_2O)_2$	3B2	17
$Eu_2(H_2O)_2(OH)_4(bdc)$	3P	18
$Eu_2(bdc)(OH)_4$	3P	18
Eu(bdc)	3P	18
$Tb_2(bdc)_3(H_2O)_4$	3P	19
$Ln_3(bdc)_{4.5}(DMF)_2(H_2O)_3$ (Ln = Tb, Dy, Ho, Er)	3Ca	20
$Ln(atp)_{1.5}(phen)(H_2O)$ (Ln = La, Eu)	2B2a	21
$Ln_2(atp)_3(phen)_2(H_2O)$ (Ln =Tb, Er)	2B2a	21
$Yb_2(OH)(atp)_{2.5}(phen)_2$	3B2	21
$Ln_3(bdc)_{3.5}(OH)_2(H_2O)_2\cdot H_2O$ (Ln = Yb, Er)	3Cb	22
$Ln_3(atp)_3(Hatp)_3\cdot 9H_2O$ (Ln=Pr, Nd)	3B3	23
$Ln_7(OH)_8(nda)_6(OH)_{0.5}(Ac)_{0.5}(H_2O)_7\cdot 4H_2O$ (Ln = Ho, Yb)	3B7	24
$Ln_2(ndc)_3(phen)_2(H_2O)_2$ (Ln = La, Eu, Ho)	2B2a	25
$Eu(bdc)_{3/2}(phen)(H_2O)$	2B2a	26
$Yb_2(bdc)_3(phen)_2(H_2O)$	2B2a	26

$Ln_2(ndc)_3(DMF)_4 \cdot H_2O$ (Ln = Nd, La)	2B2a	27
$Eu_2(ndc)_3(DMF)_4$	2B2a	27
$La_2(bdc)_3(H_2O)_2(phen)_2$	2B2a	28
$[Eu_2(bdc)_3(MeOH)_4] \cdot 8MeOH$	3B2	29
$[Ln(bdc)(MeOH)_4]Cl \cdot MeOH \cdot 0.25H_2O$ (Ln = Eu, Gd, Tb)	2B2a	29
$[Ln(bdc)NO_3(MeOH)_2] \cdot MeCN \cdot H_2O$ (Ln = Eu, Gd)	2B2a	29
$LaNa(bdc)_2(DMF)_2$	2B1a	30
$Ln_2(ndc)_3(H_2O)_2 \cdot nH_2O$ (Ln = Eu, Gd)	3Ca	31
$Ln_2(ndc)_3(bpy)_{0.5}(H_2O)_3(bpy)$ (Ln = Eu, Yb)	2B2a	31
$Nd(atp)_{1.5}(H_2O)_2 \cdot 2H_2O$	3Cb	33
$Pr_2(atp)_3(H_2O)_5 \cdot 2H_2O$	3Ca	34
$Ln(atp)_{1.5}(H_2O)_2 \cdot 2H_2O$ (Ln=Tb, Eu)	3Cb	34
$Yb_2(OH)_2(atp)_2 \cdot 0.5H_2O$	3Cb	35
$La_2(atp)_3(H_2O)_7$	3Ca	36
$Lu_2(bdc)_3(H_2O)_8 \cdot 2H_2O$	1B2	37
$Dy(atp)_{1.5}(H_2O)_2(H_2O)_2$	3Cb	38
$Ln_2(atp)_3(H_2O)_2 \cdot 0.5(bpy)(H_2O)$ (Ln = Eu, Gd, Yb)	3Cb	39
$Eu_2(bdc)_3(DEF)_2] \cdot 0.7H_2O$	3Ca	40
$Eu_2(bdc)_3(H_2O)_2(DMF)_2$	3B2	41
$Er_2(atp)_3(H_2O)_4$	3Cb	42
$Gd_2(bdc)_3(DEF)_2 \cdot H_2O$	3Ca	43
$Gd_2(atp)_3(DMF)_4$	3B2	44
$Gd_2(atp)_2(acatp)(DMF)_4 \cdot DMF$	3B2	44
$Gd_2(atp)_3(DMF)_4 \cdot DMF$	3B2	44
$Ln(bdc)_{1.5}(DEF)$ (Ln = La, Ce, Nd)	3Ca	45
$Er_2(L)_3(DMF)(H_2O) \cdot DMF$	3Ca	46
$Er_2(bdc)_3(DMF)_2(H_2O)_2 \cdot H_2O$	3B2	46

[a] bdc = 1,4-benzenedicarboxylate (*p*-phthalate, terephthalate); btp = 2-bromoterephthalate; atp = 2-aminoterephthalate; acatp = 2-acetylaminoterephthalate; nda = 1,4-naphthalenedicarboxylate; Ac = acetate; phen = 1,10-phenanthroline; bpy = 4,4'-bipiridine; mcp = pentamethyl-cyclopentadienyl; Tp = hydrogen tris(pyrazolyl)borate; DMF = dimethylformamide; DEF = diethylformamide

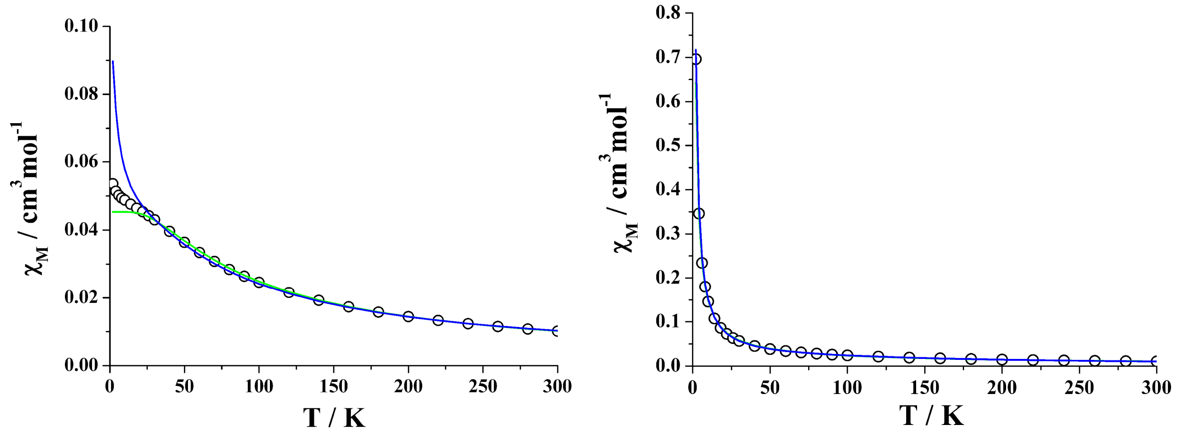
[b] references are from reference list of the main text



a) b)

c) d)

Fig. S5. Schematic views of lanthanide coordination polymers with *p*-phthalates of 3C and 2Bn type, showing possible ways of chain interconnection. Ellipses represent the chains (view along the axis of chain), rods represent benzenedicarboxylate bridges.



(a) (b)

Fig. S6 Plots of χ_M vs. T (○) along with calculated curves (green – model based on Hamiltonian ($\hat{H} = \Delta\hat{J}_z^2 + \mu_B g_J H\hat{J}$), blue – model based on Hamiltonian ($\hat{\boldsymbol{H}}_{TTP} = \boldsymbol{A}_2^0\boldsymbol{O}_2^0 + \boldsymbol{A}_4^0\boldsymbol{O}_4^0 + \boldsymbol{A}_6^0\boldsymbol{O}_6^0 + \boldsymbol{A}_6^6\boldsymbol{O}_6^6$); the green and blue lines almost coincide in some temperature ranges) for complexes (a) **1** and (b) **2**.

Formula for calculation of the formal values of Δ from crystal field parameters.

$$\Delta = 3A_2^0 - 30J(J+1)\cdot A_4^0 + \left(105J^2(J+1)^2 - 525J(J+1) + 294\right)\cdot A_6^0$$

where J is total angular momentum for the ground level of lanthanide ion.

This formula was obtained from the Hamiltonian for a tricapped trigonal prism (TTP)

$$\hat{\boldsymbol{H}}_{TTP} = \boldsymbol{A}_2^0\boldsymbol{O}_2^0 + \boldsymbol{A}_4^0\boldsymbol{O}_4^0 + \boldsymbol{A}_6^0\boldsymbol{O}_6^0 + \boldsymbol{A}_6^6\boldsymbol{O}_6^6,$$

using tabulated equations for $\boldsymbol{O}_k^q$ from [73]. Each coefficient for $\boldsymbol{A}_k^q$ in the equation for Δ is the same as the corresponding coefficient for $\hat{\boldsymbol{J}}_z^2$ in the equations from [73] for $\boldsymbol{O}_k^q$.

Ref. 73 is as in the main text: A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions; Clarendon Press, Oxford, 1970; Sec. 5.3 & Appendix-B, Table-16.*