crystals

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SUPPORTING INFORMATION FOR:

Magnetic and Luminescent Properties of Isostructural 2D-Coordination Polymers based on 2-Pyrimidinecarboxylate and Lanthanide Ions

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1. Crystallographic Data for compound 1 and 2

Table S1. Selected bond lengths (Å) for complex **1**.

Dy1-O5	2.35(3)	Dy2-O6	2.32(2)
Dy1-O8	2.33(2)	Dy2-O7	2.31(2)
Dy1-O10	2.32(3)	Dy2-O9	2.37(2)
Dy1-O11	2.81(2)	Dy2-O11	2.27(3)
Dy1-O12	2.35(2)	Dy2-O3	2.46(3)
Dy1-O1	2.40(2)	Dy2-N3	2.53(3)
Dy1-N1	2.61(2)	Dy2-O4	2.49(2)
Dy1-O2	2.43(1)	Dy2-N4	2.51(3)
Dy1-N2	2.61(2)		
Dy3-O17	2.32(2)	Dy4-O18	2.32(3)
Dy3-O19	2.32(2)	Dy4-O20	2.33(2)
Dy3-O21	2.30(2)	Dy4-O21	2.69(2)
Dy3-O23	2.76(3)	Dy4-O22	2.34(3)
Dy3-O24	2.38(2)	Dy4-O23	2.33(3)
Dy3-O13	2.45(3)	Dy4-O15	2.35(2)
Dy3-N5	2.62(3)	Dy4-N7	2.60(2)
Dy3-O14	2.33(2)	Dy4-O16	2.40(2)
Dy3-N6	2.54(3)	Dy4-N8	2.64(2)

Table S2. Selected bond lengths (Å) for complex **2**.

Nd1-O6	2.44(3)	Nd2-O5	2.38(3)
Nd1-O7	2.41(5)	Nd2-O8	2.40(3)
Nd1-O9	2.66(3)	Nd2-O9	2.45(4)
Nd1-O10	2.45(3)	Nd2-O11	2.69(5)
Nd1-O11	2.30(4)	Nd2-O12	2.49(3)
Nd1-O1	2.41(3)	Nd2-O3	2.45(3)
Nd1-N1	2.63(4)	Nd2-N3	2.62(2)
Nd1-O2	2.53(3)	Nd2-O4	2.55(3)
Nd1-N2	2.74(3)	Nd2-N4	2.75(2)
Nd3-O17	2.68(3)	Nd4-O17	2.45(3)
Nd3-O18	2.50(3)	Nd4-O19	2.74(3)
Nd3-O19	2.39(3)	Nd4-O20	2.48(3)
Nd3-O21	2.46(3)	Nd4-O22	2.42(3)
Nd3-O24	2.39(3)	Nd4-O23	2.39(3)
Nd3-O13	2.47(2)	Nd4-O15	2.55(3)
Nd3-N5	2.67(3)	Nd4-N7	2.54(2)
Nd3-O14	2.47(2)	Nd4-O16	2.56(3)
Nd3-N6	2.71(3)	Nd4-N8	2.58(2)

Table S3. Selected bond angles (°) for complex **1**.

N1-Dy1-O1	64.7(5)	N4-Dy2-O4	62.5(9)
N2-Dy1-O2	64.4(5)	N3-Dy2-O3	64.4(9)
O10-Dy1-O11	78.2(7)	O9-Dy2-O11	122.3(7)
O5-Dy1-O8	131.3(8)	O6-Dy2-O7	132.0(7)
N1-Dy1-O5	71.8(8)	N4-Dy2-O6	72.0(9)
N5-Dy3-O13	62.3(11)	N7-Dy4-O15	64.7(6)
N6-Dy3-O14	66.0(10)	N8-Dy4-O16	64.4(6)
O21-Dy3-O23	76.3(6)	O21-Dy4-O23	77.4(8)
O17-Dy3-O19	134.6(7)	O18-Dy4-O20	134.2(6)
N5-Dy3-O19	73.1(10)	N7-Dy4-O20	72.7(6)

Table S4. Selected bond angles (°) for complex **2**.

N1-Nd1-O1	61.2(10)	N4-Nd2-O4	59.5(11)
N2-Nd1-O2	62.5(9)	N3-Nd2-O3	69.7(8)
O9-Nd1-O11	78.2(12)	O9-Nd2-O11	75.5(11)
O6-Nd1-O7	137.3(13)	O5-Nd2-O8	136.2(12)
N1-Nd1-O6	74.1(11)	N4-Nd2-O5	77.0(14)
N5-Nd3-O13	63.7(8)	N8-Nd4-O16	67.9(10)
N6-Nd3-O14	62.2(8)	N7-Nd4-O15	61.7(8)
O17-Nd3-O19	76.5(10)	O17-Nd4-O19	74.5(9)
O21-Nd3-O24	133.4(12)	O22-Nd4-O23	135.0(11)
N5-Nd3-O24	68.8(9)	N8-Nd4-O23	72.1(13)

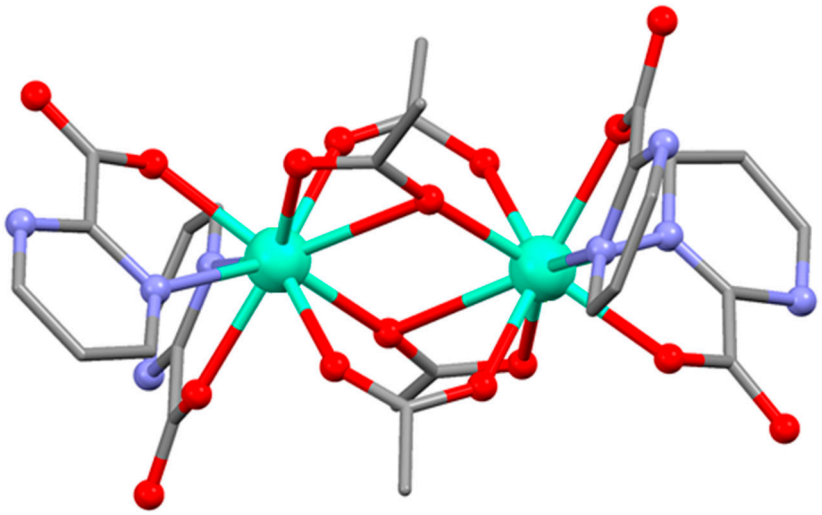

Figure S1. Perspective views of the Dy^{3+} ions in the crystal structure of **1**. Hydrogen atoms are omitted for clarity.

2. IR spectra for compound 1, 2 and ligand

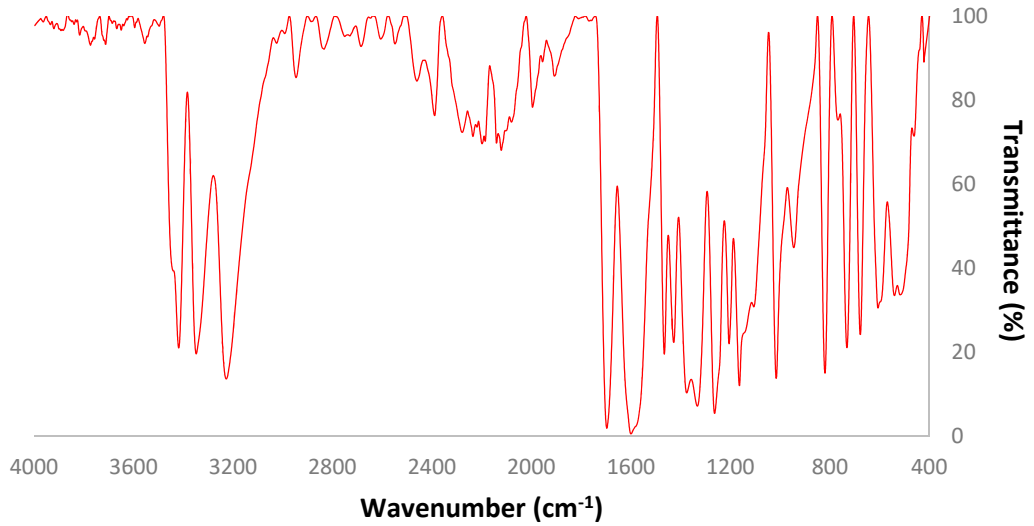

Figure S2. IR spectrum of 2-pyrimidinecarbonitrile ligand, precursor of *pymca* ligand.

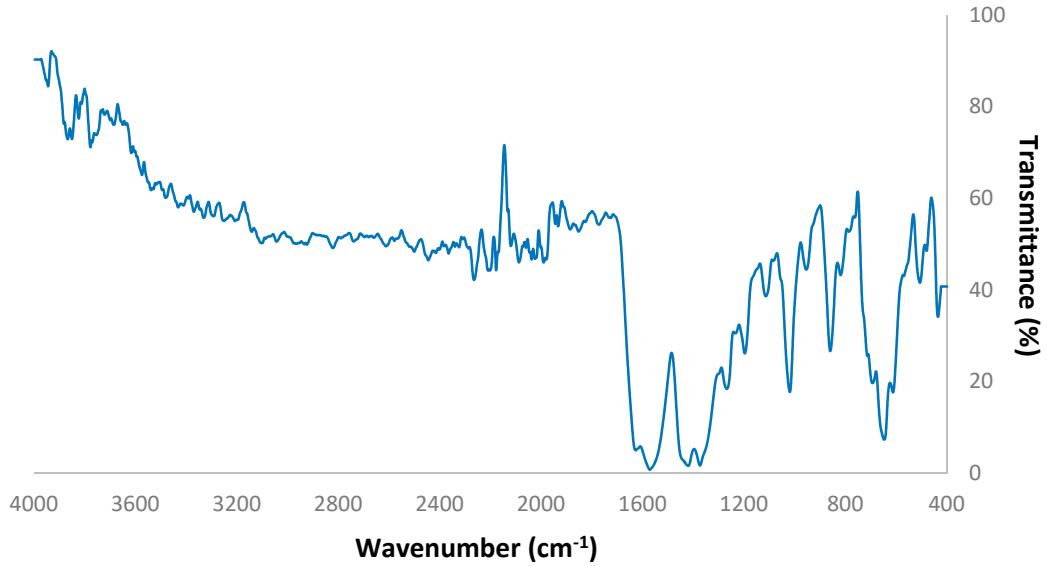

Figure S3. IR spectrum of $[Dy_4(pymca)_4(AcO)_8]_n$ (compound **1**).

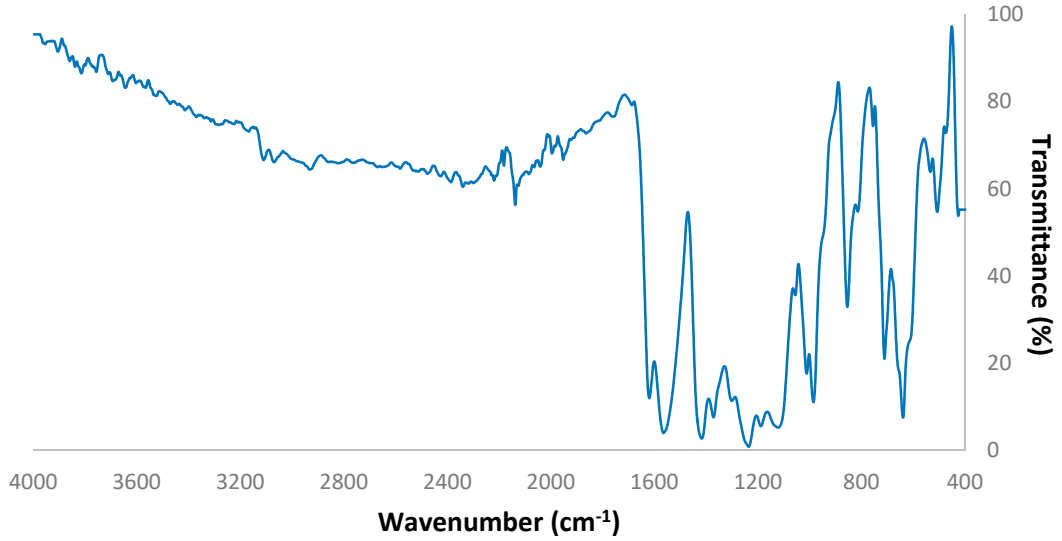

Figure S4. IR spectrum of $[Nd_4(pymca)_4(AcO)_8]_n$ (compound **2**).

3. Continuous Shape Measurements for compound 1 and 2

A continuous shape measures analysis of the coordination polyhedra of compounds **1** and **2** has been calculated with the SHAPE 2.1 program (Llunell, M.; Casanova, D.; Cirera, J.; Alemany, P.; Alvarez, S. SHAPE (2.1); Universitat de Barcelona: Barcelona, Spain, 2013). The closer the value to zero, the better fits to an ideal polyhedron. The analysis of CShMs for these compounds revealed that all metal centres exhibit nine-coordinated environments (see Table S5) except for Dy2 atom, which shows an eight-centred polyhedron (Table S6). This difference is derived from a semi-coordination of the bridging acetate ligand, in such a way that it forms a coordination bond with Nd2 atom but not with Dy2 atom due to the larger ion size of Nd(III) ion compared to Dy(III).

Table S5. Continuous Shape Measurements for compounds **1** and **2** considering a coordination number of 9.

EP-9	D9h	Enneagon
OPY-9	C8v	Octagonal pyramid
HBPY-9	D7h	Heptagonal bipyramid
JTC-9	C3v	Johnson triangular cupola J3
JCCU-9	C4v	Capped cube J8
CCU-9	C4v	Spherical-relaxed capped cube
JCSAPR-9	C4v	Capped square antiprism J10
CSAPR-9	C4v	Spherical capped square antiprism
JTCTPR-9	D3h	Tricapped trigonal prism J51
TCTPR-9	D3h	Spherical tricapped trigonal prism
JTDIC-9	C3v	Tridiminished icosahedron J63
HH-9	C2v	Hula-hoop
MFF-9	Cs	Muffin

Structure [ML9]	EP-9	OPY-9	HBPY-9	JTC-9	JCCU-9	CCU-9	JCSAPR-9
Comp1 Dy1	33.886	22.646	17.678	13.885	8.933	8.991	1.589
Comp1 Dy2	33.721	22.382	17.473	14.006	9.565	9.525	1.696
Comp1 Dy3	34.553	23.116	18.216	14.249	10.677	10.248	1.783
Comp1 Dy4	34.746	23.080	17.699	14.766	8.729	9.216	1.613
Comp2 Nd1	34.464	22.666	18.408	13.822	11.046	9.882	2.170
Comp2 Nd2	33.650	21.495	17.026	14.561	9.712	9.321	1.816
Comp2 Nd3	33.750	23.435	17.081	13.226	8.623	8.079	2.185
Comp2 Nd4	36.281	22.262	16.794	15.473	9.092	8.717	1.681

Structure [ML9]	CSAPR-9	JTCTPR-9	TCTPR-9	JTDIC-9	HH-9	MFF-9
Comp1 Dy1	1.677	2.163	2.417	13.723	10.860	**1.254**
Comp1 Dy2	1.659	2.087	2.425	13.879	9.616	**1.249**
Comp1 Dy3	1.614	2.017	2.203	13.893	9.783	**1.132**
Comp1 Dy4	2.080	2.773	2.926	13.695	10.722	**1.510**
Comp2 Nd1	1.756	2.284	2.206	13.560	9.706	**1.354**
Comp2 Nd2	1.431	2.572	2.573	13.989	9.137	**0.952**
Comp2 Nd3	1.763	2.434	2.408	12.758	10.508	**1.312**
Comp2 Nd4	1.390	3.400	2.421	12.675	9.200	**0.932**

Table S6. Continuous Shape Measurements for Dy2 in compound **1**, considering its eight-coordination.

OP-8	D8h	Octagon
HPY-8	C7v	Heptagonal pyramid
HBPY-8	D6h	Hexagonal bipyramid
CU-8	Oh	Cube
SAPR-8	D4d	Square antiprism
TDD-8	D2d	Triangular dodecahedron
JGBF-8	D2d	Johnson gyrobifastigium J26
JETBPY-8	D3h	Johnson elongated triangular bipyramid J14
JBTPR-8	C2v	Biaugmented trigonal prism J50
BTPR-8	C2v	Biaugmented trigonal prism
JSD-8	D2d	Snub diphenoid J84
TT-8	Td	Triakis tetrahedron
ETBPY-8	D3h	Elongated trigonal bipyramid

Structure [ML8]	**OP-8**	**HPY-8**	**HBPY-8**	**CU-8**	**SAPR-8**	**TDD-8**	**JGBF-8**
Comp1 Dy2	29.259	23.012	14.742	9.391	**0.810**	2.554	13.757

Structure [ML8]	**JETBPY-8**	**JBTPR-8**	**BTPR-8**	**JSD-8**	**TT-8**	**ETBPY-8**
Comp1 Dy2	27.954	2.238	1.579	4.653	10.177	23.808

4. Magnetic measurements for compound 1

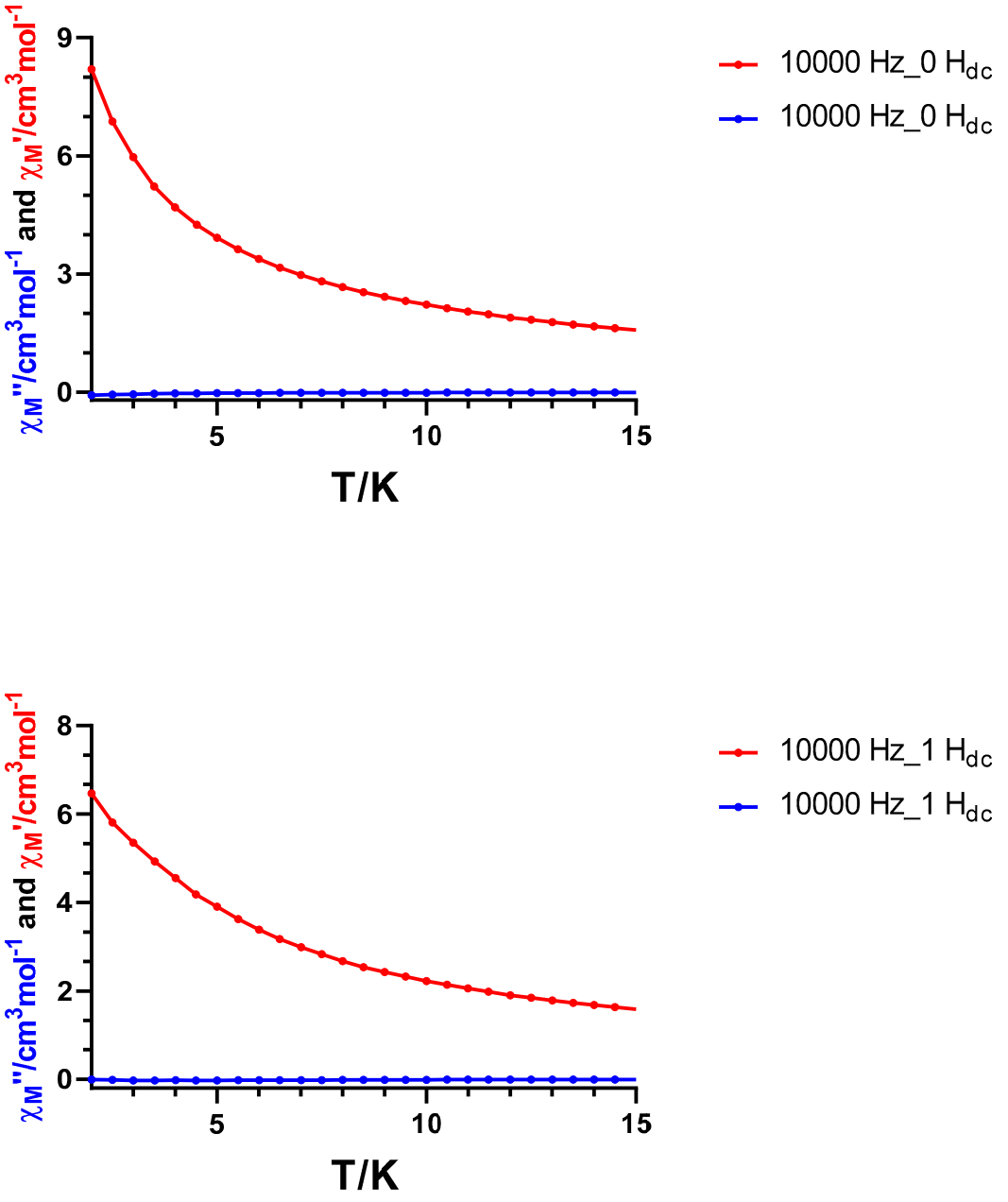

Figure S5. Temperature dependence of in-phase (red) and out-of-phase (blue) components of the *ac* susceptibility in a zero (top) and under 1 kOe applied *dc* field (down) for **1**.

5. Photoluminescence measurements

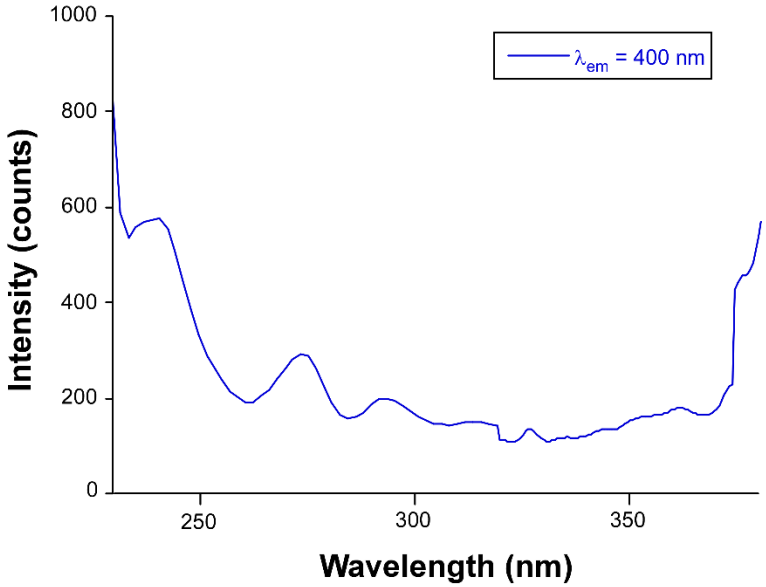

Figure S6. Excitation spectrum for the ligand sample.