## SUPPORTING INFORMATION

Highly optically diluted lanthanide coordination polymers with unexpected strong luminescence.

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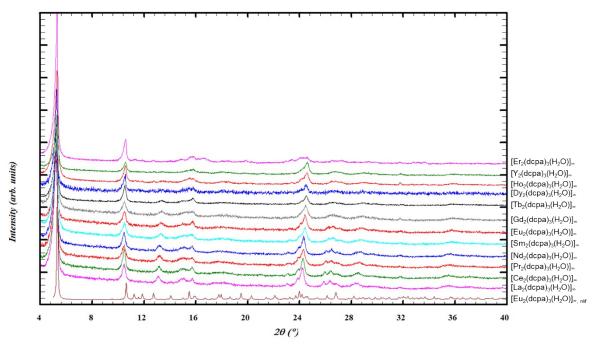
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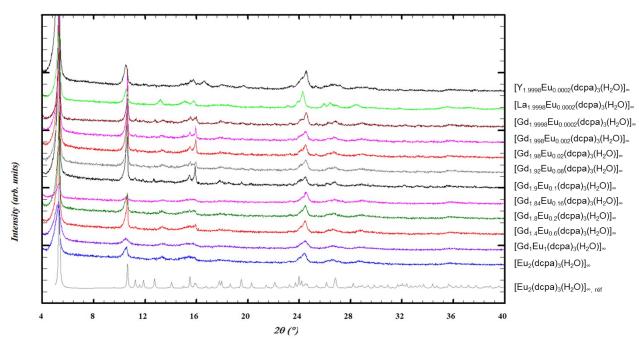
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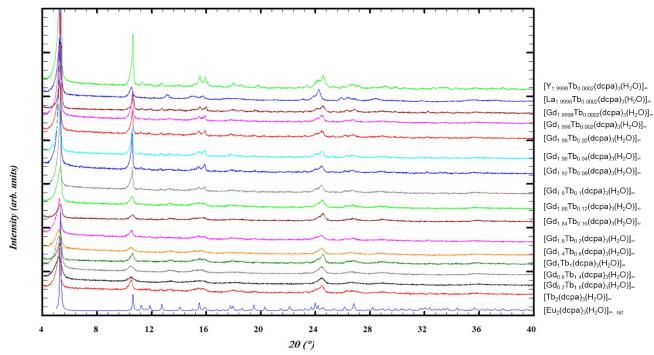
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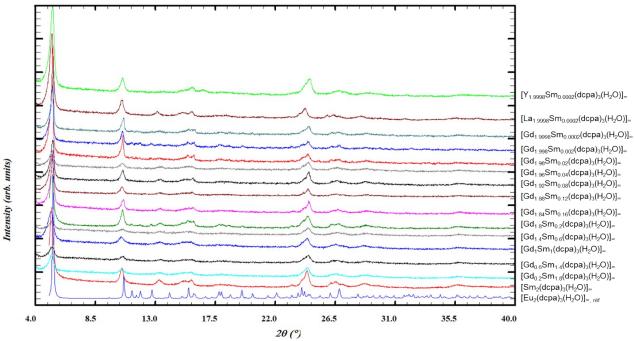
**Figure S1.** Experimental X-ray powder diffraction diagrams of  $[Ln_2(dcpa)_3(H_2O)]_{\infty}$  with Ln = La-Er except Pm plus Y and simulated powder diffraction pattern of  $[Eu_2(dcpa)_3(H_2O)]_{\infty}$  from its crystal structure (CCDC-1551529).



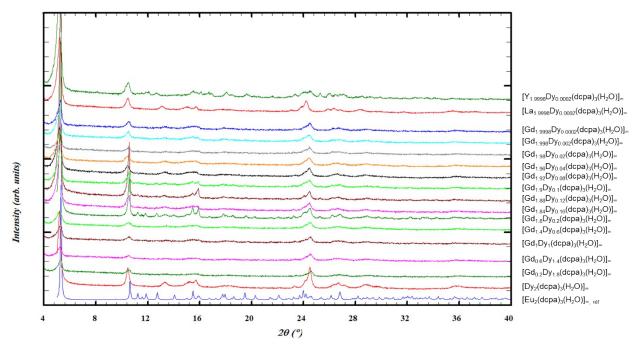
**Figure S2.** Experimental X-ray powder diffraction diagrams of  $[Gd_{2-2x}Eu_{2x}(dcpa)_3(H_2O)]_{\infty}$  with  $0.0001 \le x \le 1$ ,  $[La_{2-2x}Eu_{2x}(dcpa)_3(H_2O)]_{\infty}$  and  $[Y_{2-2x}Eu_{2x}(dcpa)_3(H_2O)]_{\infty}$  with x = 0.0001 and simulated powder diffraction pattern of  $[Eu_2(dcpa)_3(H_2O)]_{\infty}$  from its crystal structure (CCDC-1551529).



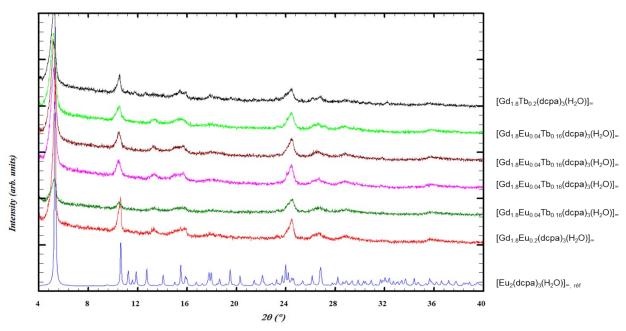
**Figure S3.** Experimental X-ray powder diffraction diagrams of  $[Gd_{2-2x}Tb_{2x}(dcpa)_3(H_2O)]_{\infty}$  with  $0.0001 \le x \le 1$ ,  $[La_{2-2x}Tb_{2x}(dcpa)_3(H_2O)]_{\infty}$  and  $[Y_{2-2x}Tb_{2x}(dcpa)_3(H_2O)]_{\infty}$  with x = 0.0001 and simulated powder diffraction pattern of  $[Eu_2(dcpa)_3(H_2O)]_{\infty}$  from its crystal structure (CCDC-1551529).



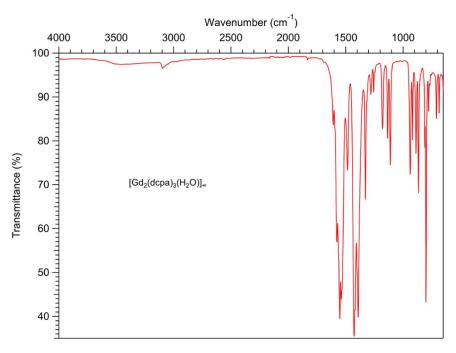
**Figure S4.** Experimental X-ray powder diffraction diagrams of  $[Gd_{2-2x}Sm_{2x}(dcpa)_3(H_2O)]_{\infty}$  with  $0.0001 \le x \le 1$ ,  $[La_{2-2x}Sm_{2x}(dcpa)_3(H_2O)]_{\infty}$  and  $[Y_{2-2x}Sm_{2x}(dcpa)_3(H_2O)]_{\infty}$  with x = 0.0001 and simulated powder diffraction pattern of  $[Eu_2(dcpa)_3(H_2O)]_{\infty}$  from its crystal structure (CCDC-1551529).



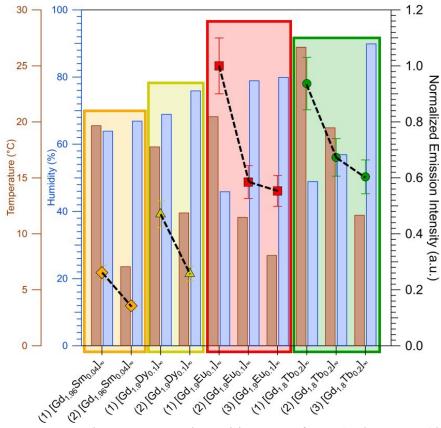
**Figure S5.** Experimental X-ray powder diffraction diagrams of  $[Gd_{2-2x}Dy_{2x}(dcpa)_3(H_2O)]_{\infty}$  with  $0.0001 \le x \le 1$ ,  $[La_{2-2x}Dy_{2x}(dcpa)_3(H_2O)]_{\infty}$  and  $[Y_{2-2x}Dy_{2x}(dcpa)_3(H_2O)]_{\infty}$  with x = 0.0001 and simulated powder diffraction pattern of  $[Eu_2(dcpa)_3(H_2O)]_{\infty}$  from its crystal structure (CCDC-1551529).



**Figure S6.** Experimental X-ray powder diffraction diagrams of  $[Gd_{1.8}Eu_{0.2-0.2x}Tb_{0.2x}(dcpa)_3(H_2O)]_{\infty}$  with  $0 \le x \le 1$  and simulated powder diffraction pattern of  $[Eu_2(dcpa)_3(H_2O)]_{\infty}$  from its crystal structure (CCDC-1551529).



**Figure S7.** Solid state IR spectrum of [Gd<sub>2</sub>(dcpa)<sub>3</sub>(H<sub>2</sub>O)]<sub>∞</sub>.



**Figure S8.** Luminescence intensities of  $[Gd_{1.96}Sm_{0.04}(dcpa)_3(H_2O)]_{\infty}$ ,  $[Gd_{1.9}Dy_{0.1}(dcpa)_3(H_2O)]_{\infty}$ ,  $[Gd_{1.80}Eu_{0.2}(dcpa)_3(H_2O)]_{\infty}$  and  $[Gd_{1.8}Tb_{0.2}(dcpa)_3(H_2O)]_{\infty}$ , *versus* climatic conditions during the preparation of the microcrystalline powders. The numbers (1), (2) and (3) refer to different samples.

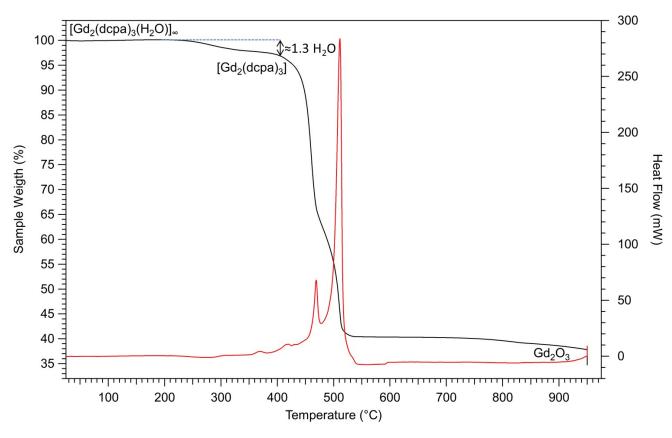
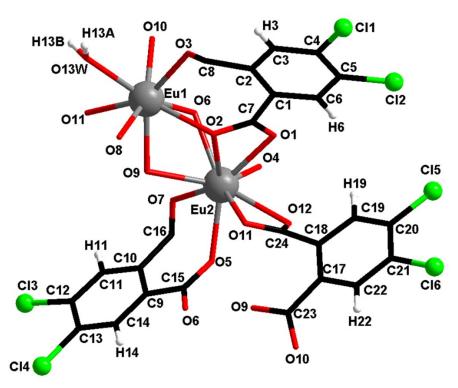
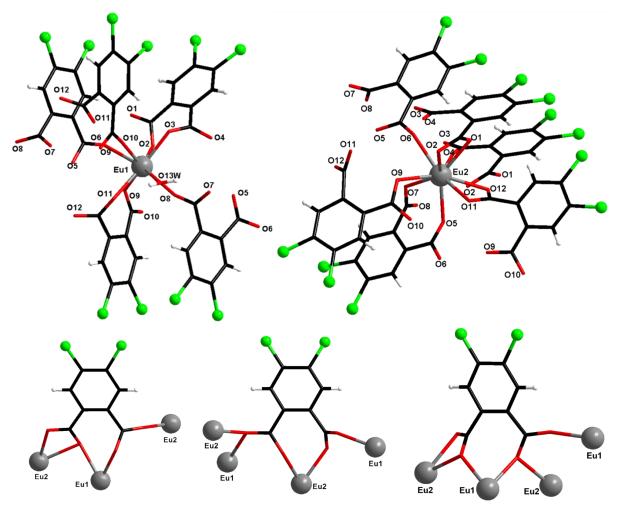


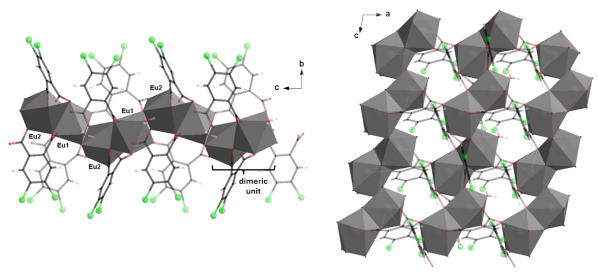
Figure S9. Thermal analysis of  $[Gd_2(dcpa)_3(H_2O)]_{\infty}$  under air flux in a platinum crucible.



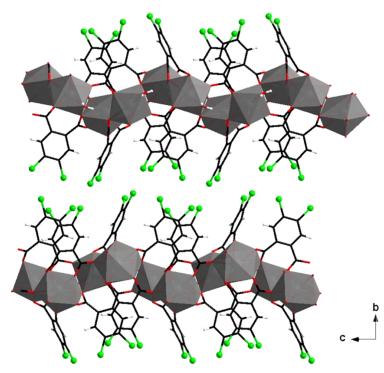
**Figure S10.** Projection view of an extended asymmetric unit of  $[Eu_2(dcpa)_3(H_2O)]_{\infty}$  with the numbering scheme.



**Figure S11.** Lanthanide ions environments (top) and coordination modes of the dcpa<sup>2-</sup> ligands (bottom) in  $[Eu_2(dcpa)_3(H_2O)]_{\infty}$ .



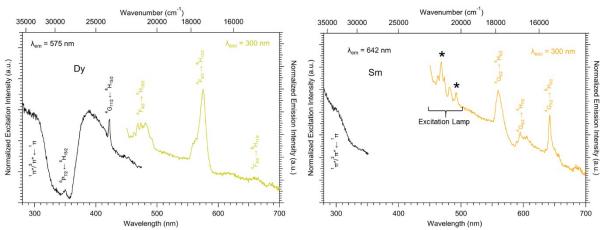
**Figure S12.** Projection views along the *a*- and *b*-axis of a chain-like molecular motif (left) and of a bidimensional molecular motif (right) of  $[Eu_2(dcpa)_3(H_2O)]_{\infty}$ .



**Figure S13.** Projection view along the *a*-axis of two adjacent molecular planes of  $[Eu_2(depa)_3(H_2O)]_{\infty}$ .

**Table S1.** Mean distance between emissive lanthanide ions *versus* the doping rate in molecular alloys of general chemical formula  $[Ln_{2x}Ln'_{2-2x}(dcpa)_3(H_2O)]_{\infty}$ .

Doping rate of emissive ions (%)	Mean distance between emissive lanthanide	
Doping rate of emissive ions (70)		
	ions (Å)	
0.01	95.2	
0.1	44.2	
0.5	25.5	
1	20.5	
2	17.3	
4	13.6	
5	11.4	
6	10.5	
8	9.5	
10	8.9	
20	6.0	
30	5.5	
40	4.8	
50	4.2	
60	4.1	
70	4.0	
80	3.9	
90	3.9	
100	3.8	



**Figure S14.** Room temperature solid-state excitation and emission spectra of  $[Ln_2(dcpa)_3(H_2O)]_{\infty}$  with Ln = Dy (left) and Sm (right). Stars indicate emission peaks due to the excitation lamp.

<b>Table S2.</b> O-O distances in $[Eu_2(dcpa)_3(H_2O)]_{\infty}$ .				
Atom1	Atom2	Symmetry	Distance (Å)	
O13W	O11	x, y, z	2.8396(34)	
	O8	1+x, $1/2-y$ , $1/2+z$	2.8759(33)	
	O7	1+x, $1/2-y$ , $1/2+z$	2.9153(29)	
	O5	1+x, y, z	2.9767(35)	
	O2	x, 1/2-y, -1/2+z	2.9904(30)	
	O10	x, 1/2-y, -1/2+z	3.0104(33)	
	O8	1+x, y, z	3.0885(33)	
	O3	x, y, z	3.2396(35)	

Table S3. Cl-Cl distan	ces in [Eu <sub>2</sub> (dcpa) <sub>3</sub> (H	$[2O]_{\infty}$ .	
Atom1	Atom2	Symmetry	Distance (Å)
C11	Cl2	x, y, z	3.1765(15)
C12	Cl1	x, y, z	3.1765(15)
	Cl6	2-x, $-1/2+y$ , $3/2-z$	3.3464(14)
	Cl4	1-x, -y, 1-z	3.4222(15)
C13	Cl4	x, y, z	3.1867(13)
C14	C13	x, y, z	3.1866(13)
	C15	1-x, $-1/2+y$ , $1/2-z$	3.3280(14)
	C12	1-x, -y, 1-z	3.4218(15)
C15	Cl6	x, y, z	3.1644(12)
	Cl4	1-x, $1/2+y$ , $1/2-z$	3.3294(14)
C16	C15	x, y, z	3.1651(12)
	C12	2-x, $1/2+y$ , $3/2-z$	3.3461(14)