Electronic Supplementary Material (ESI) for CrystEngComm.

Mechanochemically synthesized crystalline luminescent 2D coordination polymers of La^{3+} and Ce^{3+}, doped with Sm^{3+}, Eu^{3+}, Tb^{3+}, and Dy^{3+}: synthesis, crystal structures and luminescence

Parviz Gohari Derakhshandeh[a,b,c], Janet Soleimannejad[c], Jan Janczak[d], Anna M. Kaczmarek[a], Kristof Van Hecke*[b], Rik Van Deun*[a]

[a] L^3 – Luminescent Lanthanide Lab, Department of Inorganic and Physical Chemistry, Ghent University (UGent), Krijgslaan 281 – Building S3, B-9000 Ghent, Belgium

[b] XStruct, Department of Inorganic and Physical Chemistry, Ghent University (UGent), Krijgslaan 281 – Building S3, B-9000 Ghent, Belgium

[c] School of Chemistry, College of Science, University of Tehran, P.O. Box 14155-6455, Tehran, Iran

[d] Institute of Low Temperture and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław, Poland

Supporting Information

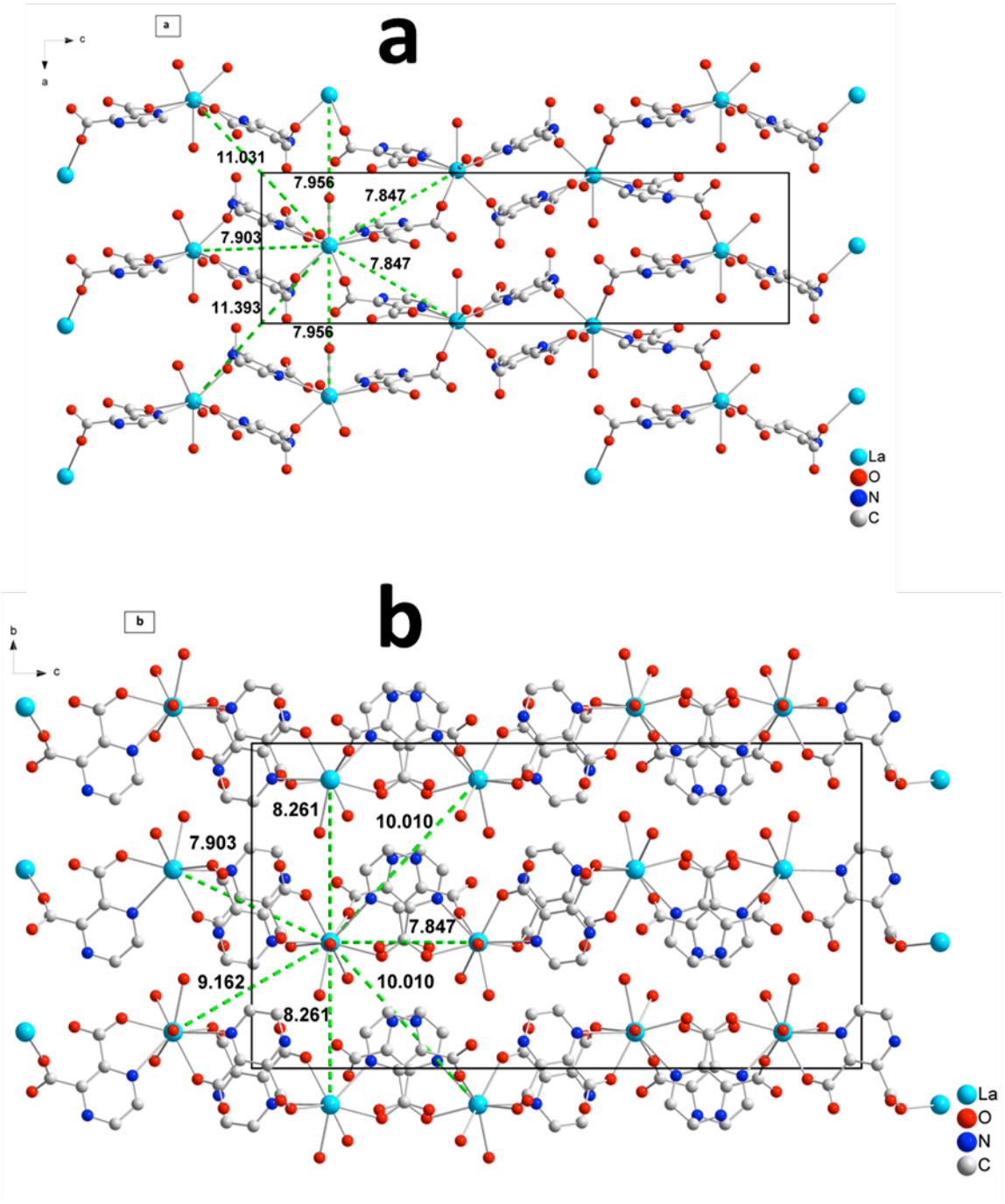

Fig.S1. Intermetallic distances between La atoms that belong to a 2D layer (a) and to different 2D layers (b) in $[La(pzdc)(Hpzdc)(H_2O)_3]_n$

(for compound **2** the Ce-Ce values are slightly shorter (~0.02Å))

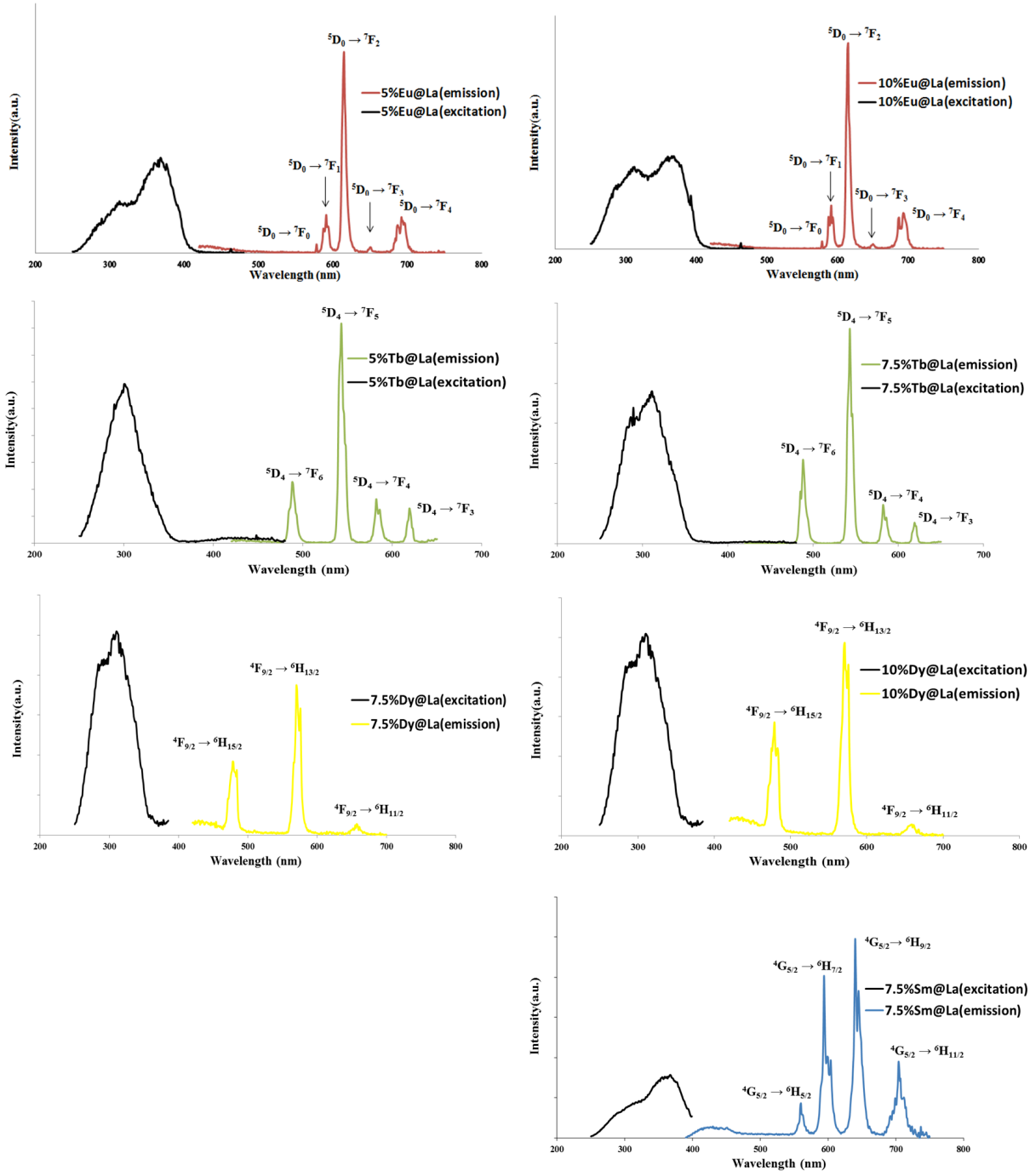

Fig. S2. Excitation and emission spectra for $[La_{1-x}Ln'_x(pzdc)(Hpzdc)(H_2O)_3]_n$, where Ln′ = Sm^{3+}, Eu^{3+}, Tb^{3+}, or Dy^{3+} and x = 0.050, 0.075 or 0.100.

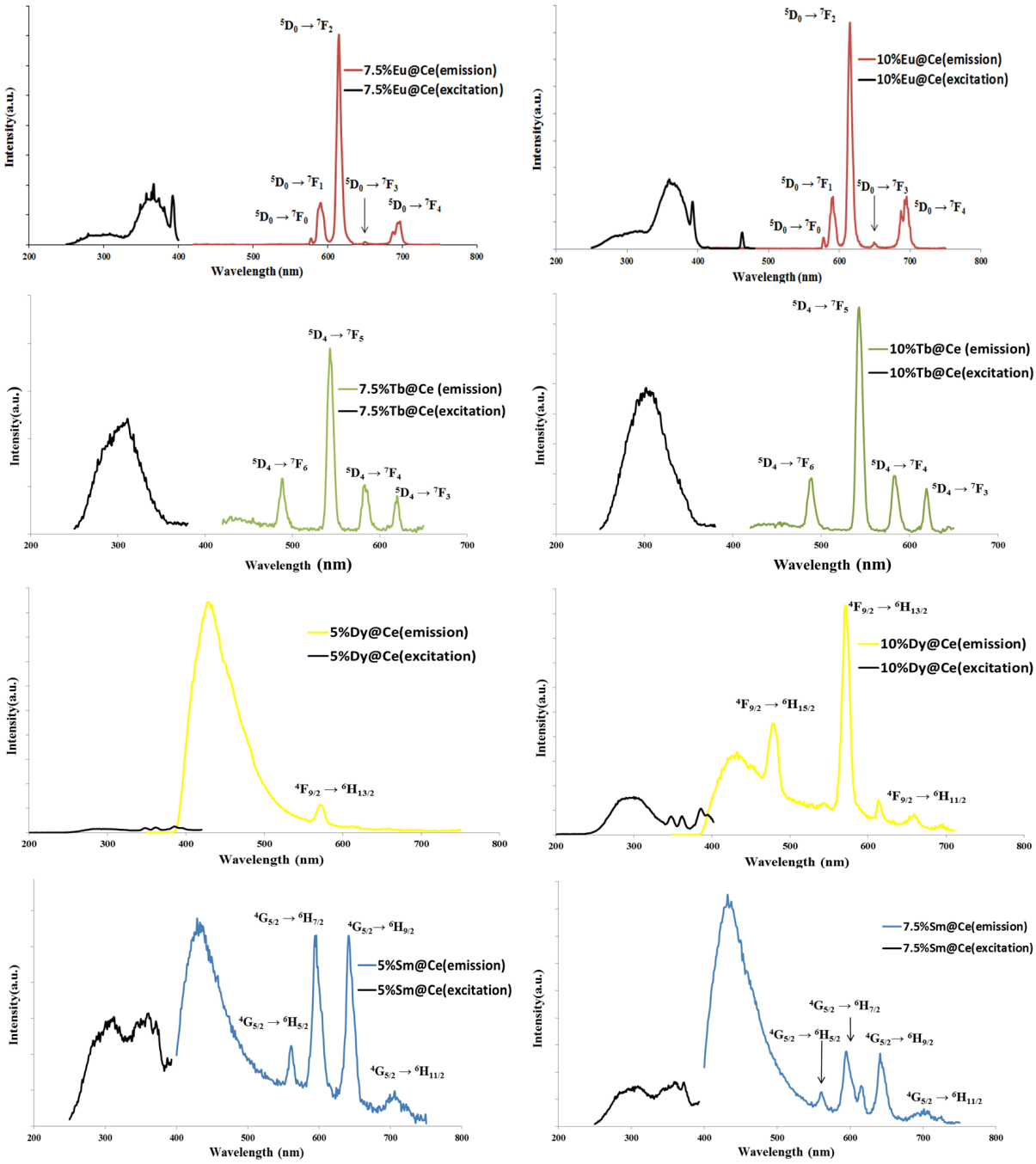

Fig. S3. Excitation and emission spectra for $[Ce_{1-x}Ln'_x(pzdc)(Hpzdc)(H_2O)_3]_n$, where Ln′ = Sm^{3+}, Eu^{3+}, Tb^{3+}, or Dy^{3+} and x = 0.050, 0.075 or 0.100.

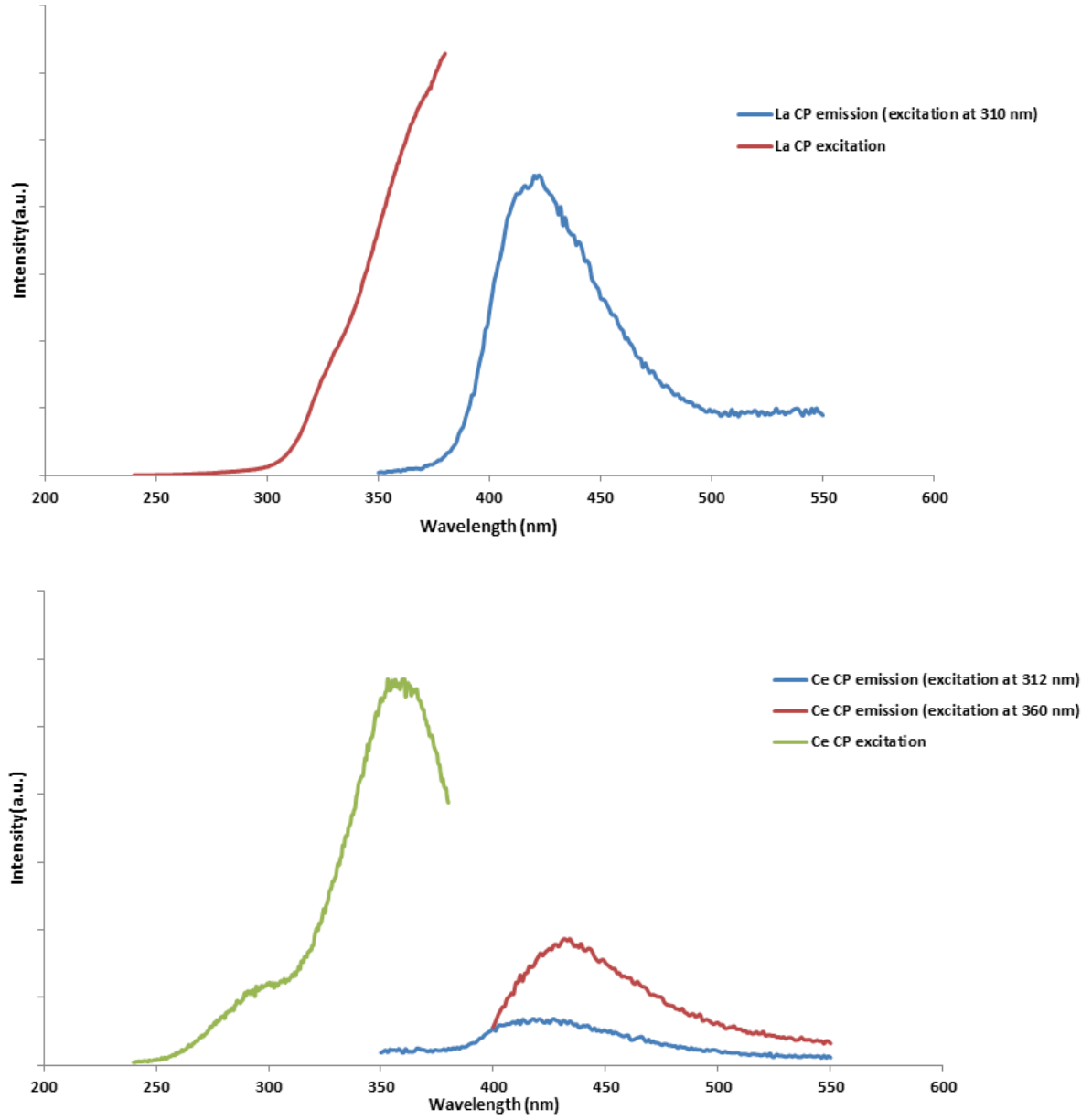

Fig. S4. Excitation and emission spectra for $[La(pzdc)(Hpzdc)(H_2O)_3]_n$, (compound **1**, top graph) and for $[Ce(pzdc)(Hpzdc)(H_2O)_3]_n$, (compound **2**, bottom graph).

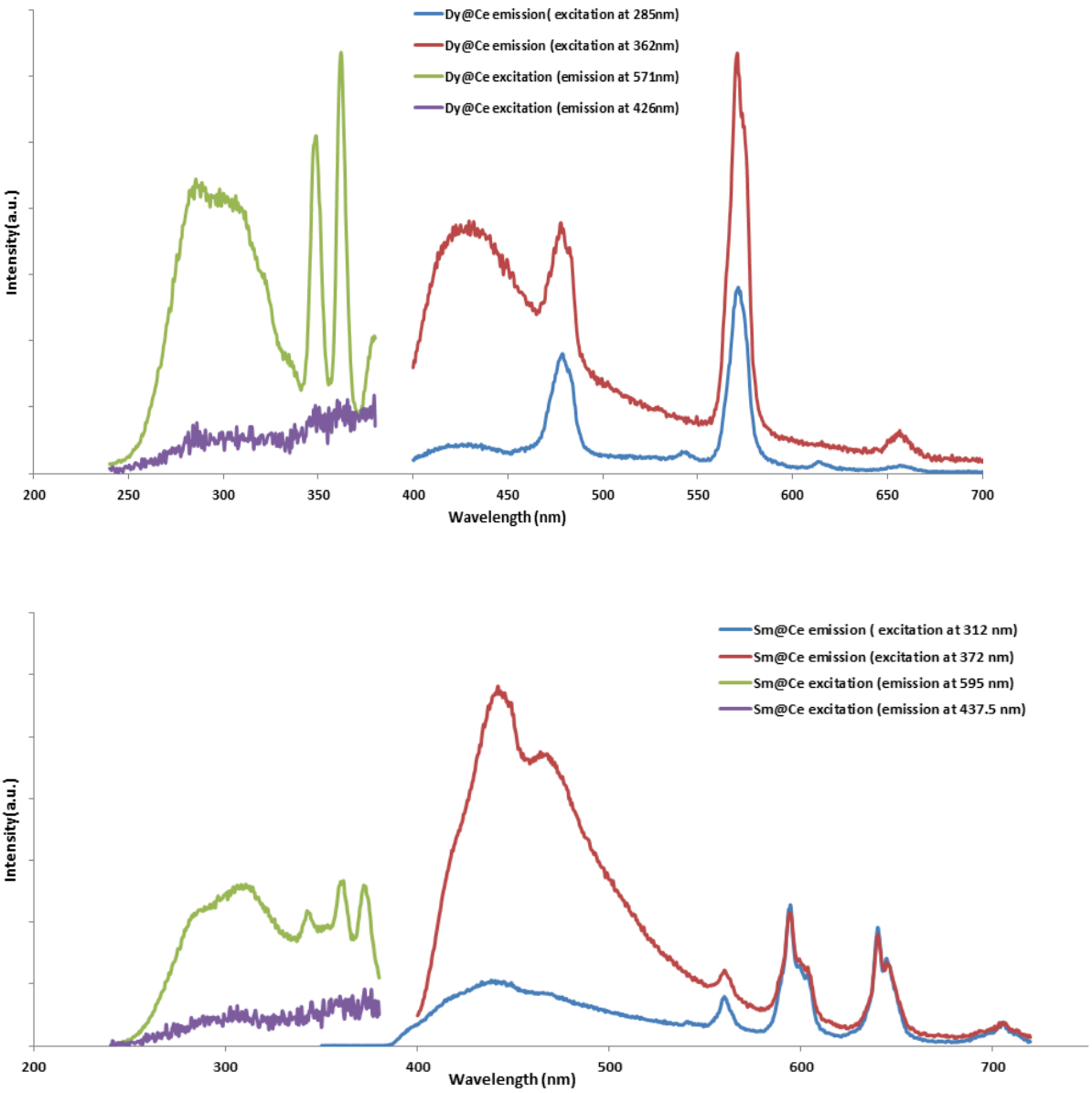

Fig. S5. Excitation and emission spectra for $[Ce_{0.925}Dy_{0.075}(pzdc)(Hpzdc)(H_2O)_3]_n$, (7.5%Dy@Ce, top graph) and for $[Ce_{0.900}Sm_{0.100}(pzdc)(Hpzdc)(H_2O)_3]_n$, (10%Sm@Ce, bottom graph).

Table S1. Selected bond lengths [Å] and angles [°] for $[Ln(pzdc)(Hpzdc)(H_2O)_3]_n$ (Ln = La (**1**) and Ce (**2**)).

Bond (Å)	**(1)**		**(2)**
La−O3^{i}	2.451(2)	Ce−O3^{i}	2.4283 (16)
La−O12	2.462(2)	Ce−O12	2.4382(15)
La−O2	2.477(2)	Ce−O2	2.4493(15)
La−O14^{ii}	2.462(2)	Ce−O14^{ii}	2.4600(15)
La−N11	2.872(2)	Ce−N11	2.8502(18)
La−O5	2.518(2)	Ce−O5	2.4970(17)
La−O6	2.524(2)	Ce−O6	2.5050(16)
La−O7	2.615(2)	Ce−O7	2.5954(17)
La−N1	2.820(2)	Ce−N1	2.7982(18)
Angle (°)			
O2−La−O6	83.40(7)	O2−Ce−O6	83.86(6)
O14^{ii}−La−O6	87.26(7)	O14^{ii}−Ce−O6	87.22(6)
O3^{ii}−La−O6	139.39(7)	O3^{ii}−Ce−O6	139.28(6)
O5−La−O6	74.43(8)	O5−Ce−O6	74.45(7)
O3^{i}−La−O7	71.23(7)	O3^{i}−Ce−O7	71.25(5)
O12−La−O7	144.91(7)	O12−Ce−O7	144.89(6)
O5−La−O7	134.05(8)	O5−Ce−O7	133.92(6)
O2−La−O7	71.69(7)	O2−Ce−O7	71.56(6)
O3^{i}−La−O2	86.90(7)	O3^{i}−Ce−O2	87.06(6)
O3^{i}−La−O14^{ii}	76.13(7)	O3^{i}−Ce−O14^{ii}	76.43(6)
O2−La−O14^{ii}	142.57(6)	O2−Ce−O14^{ii}	142.59(6)
O12−La−O5	80.98(7)	O12−Ce−O5	81.13(6)
O14^{ii}−La−O5	133.26(7)	O14^{ii}−Ce−O5	133.22(6)
O6−La−O7	68.36(7)	O6−Ce−O7	68.21(6)
O12−La−O6	134.28(7)	O12−Ce−O6	134.38(5)
O12−La−N1	68.89(7)	O12−Ce−N1	68.73(5)
O2−La−N1	59.84(7)	O2−Ce−N1	60.37(5)
O14^{ii}−La−N1	135.25(6)	O14^{ii}−Ce−N1	135.62(5)
O14^{ii}−La−O7	71.32(7)	O14^{ii}−Ce−O7	71.38(5)
O3^{i}−La−O12	80.44(7)	O3^{i}−Ce−O12	80.54(5)
O12−La−O2	127.92(7)	O12−Ce−O2	128.33(5)
O12−La−O14^{ii}	82.29(7)	O12−Ce−O14^{ii}	82.20(5)
O3^{i}−La−O5	141.96(8)	O3^{i}−Ce−O5	141.86(6)

*S*ymmetry code: (*i*) x-1/2,y,-z+1/2; (*ii*) -x,-y+2,-z; (*iii*) x+1/2,y,-z+1/2

Table S2. Hydrogen bonds geometry (Å, °) for $[Ln(pzdc)(Hpzdc)(H_2O)_3]_n$ (Ln = La (**1**) and Ce (**2**)).

(**1**)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H51···O1^{i}	0.82 (1)	1.93 (1)	2.733 (3)	167 (4)
O5—H52···O13^{ii}	0.82 (1)	1.95 (1)	2.766 (3)	173 (4)
O6—H61···O11^{iii}	0.82 (1)	1.91 (1)	2.703 (3)	163 (4)
O6—H62···O4^{iv}	0.82 (1)	1.93 (1)	2.731 (3)	167 (4)
O7—H71···O1^{v}	0.82 (1)	2.05 (1)	2.852 (3)	167 (4)
O7—H72···N4^{iv}	0.82 (1)	2.04 (1)	2.860 (3)	177 (4)
N14—H14···O4^{vi}	0.87 (1)	1.75 (1)	2.612 (3)	171 (3)

Symmetry codes: (*i*) *x*+1/2, *y*, −*z*+1/2; (*ii*) −*x*+1, −*y*+2, −*z*; (*iii*) −*x*+1/2, *y*−1/2, *z*; (*iv*) −*x*, *y*−1/2, −*z*+1/2; (*v*) *x*−1/2, *y*, −*z*+1/2; (*vi*) −*x*+1/2, −*y*+2, *z*−1/2.

(**2**)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H51···O1^{i}	0.82 (2)	1.93 (2)	2.734 (2)	167 (3)
O5—H52···O13^{ii}	0.82 (2)	1.96 (2)	2.777 (3)	173 (3)
O6—H61···O11^{iii}	0.82 (2)	1.92 (2)	2.714 (2)	162 (3)
O6—H62···O4^{iv}	0.82 (2)	1.96 (2)	2.737 (2)	158 (3)
O7—H71···O1^{v}	0.82 (2)	2.06 (2)	2.862 (2)	168 (3)
O7—H72···N4^{iv}	0.82 (2)	2.05 (2)	2.865 (3)	179 (3)
N14—H14···O4^{vi}	0.87 (2)	1.74 (2)	2.611 (2)	176 (2)

Symmetry codes: (*i*) *x*+1/2, *y*, −*z*+1/2; (*ii*) −*x*+1, −*y*+2, −*z*; (*iii*) −*x*+1/2, *y*−1/2, *z*; (*iv*) −*x*, *y*−1/2, −*z*+1/2; (*v*) *x*−1/2, *y*, −*z*+1/2; (*vi*) −*x*+1/2, −*y*+2, *z*−1/2.

Table S3. Decay times of the Ln@La and Ln@Ce (Ln = Sm^{3+}, Eu^{3+}, Tb^{3+}, or Dy^{3+}) (all values recorded for solid state samples)

Sample	Decay time [μs]	Sample	Decay time [μs]
La		Ce	
Tb@La5%	811	Tb@Ce5%	739
Tb@La7.5%	822	Tb@Ce7.5%	646
Tb@La10%	817	Tb@Ce10%	727
Eu@La5%	406	Eu@Ce5%	848
Eu@La7.5%	719	Eu@Ce7.5%	152
Eu@La10%	393	Eu@Ce10%	197
Dy@La5%	14.2	Dy@Ce5%	12.4
Dy@La7.5%	14.1	Dy@Ce7.5%	12.7
Dy@La10%	13.4	Dy@Ce10%	12.6
Sm@La5%	30.0	Sm@Ce5%	12.4
Sm@La7.5%	27.3	Sm@Ce7.5%	12.4
Sm@La10%	34.0	Sm@Ce10%	13.6