Electronic Supplementary Material (ESI) for CrystEngComm.

Polymorphism and luminescent properties of heteropolynuclear metal organic frameworks containing oxydiacetate as linker

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Supporting Information

CIE Calculation

The x and y CIE coordinates were calculated by Equations S1a and S1b from their X, Y and Z tristimulus, from Equations S2a to S2c, using photoluminescence spectral data in acetonitrile at 298 K. The numerical values of the CIE standard $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$, are available as online free-access tables[1].

$$x = \frac{X}{X+Y+Z} \qquad \text{(Eq. S1a)}$$

$$y = \frac{Y}{X+Y+Z} \qquad \text{(Eq. S1b)}$$

$$X = \int_{380}^{780} I(\lambda)\bar{x}(\lambda)\mathrm{d}\lambda \quad \text{(Eq. S2a)}$$

$$Y = \int_{380}^{780} I(\lambda)\bar{y}(\lambda)\mathrm{d}\lambda \quad \text{(Eq. S2b)}$$

$$Z = \int_{380}^{780} I(\lambda)\bar{z}(\lambda)\mathrm{d}\lambda \quad \text{(Eq. S2c)}$$

Supplementary figures

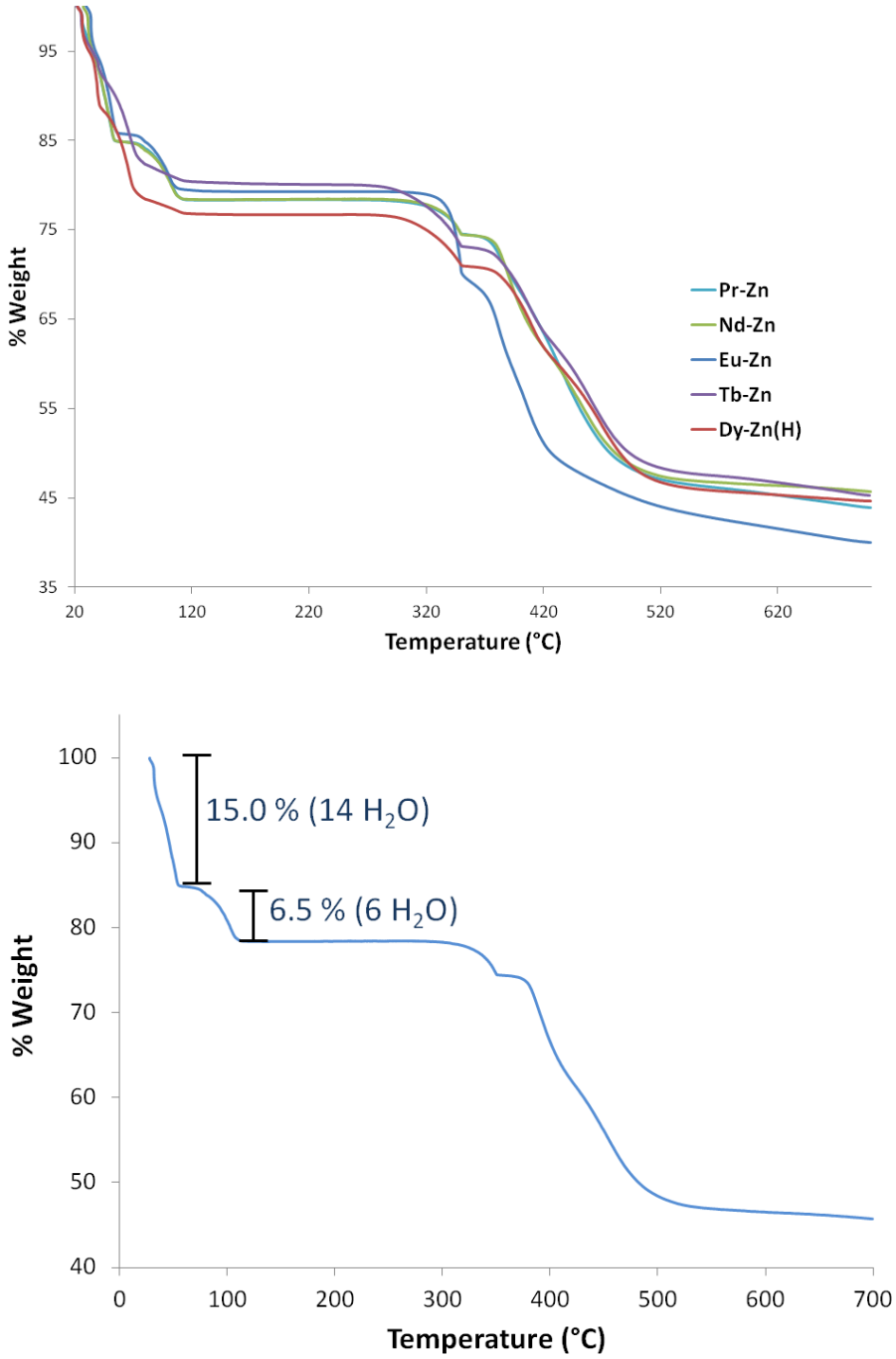


Figure S1. TGA curves for the **Ln-Zn**MOFs belonging to the hexagonal P6/mcc space group. In detail the corresponding profile for $[Nd_2Zn_3(oda)_6(H_2O)_6]\cdot 14H_2O$

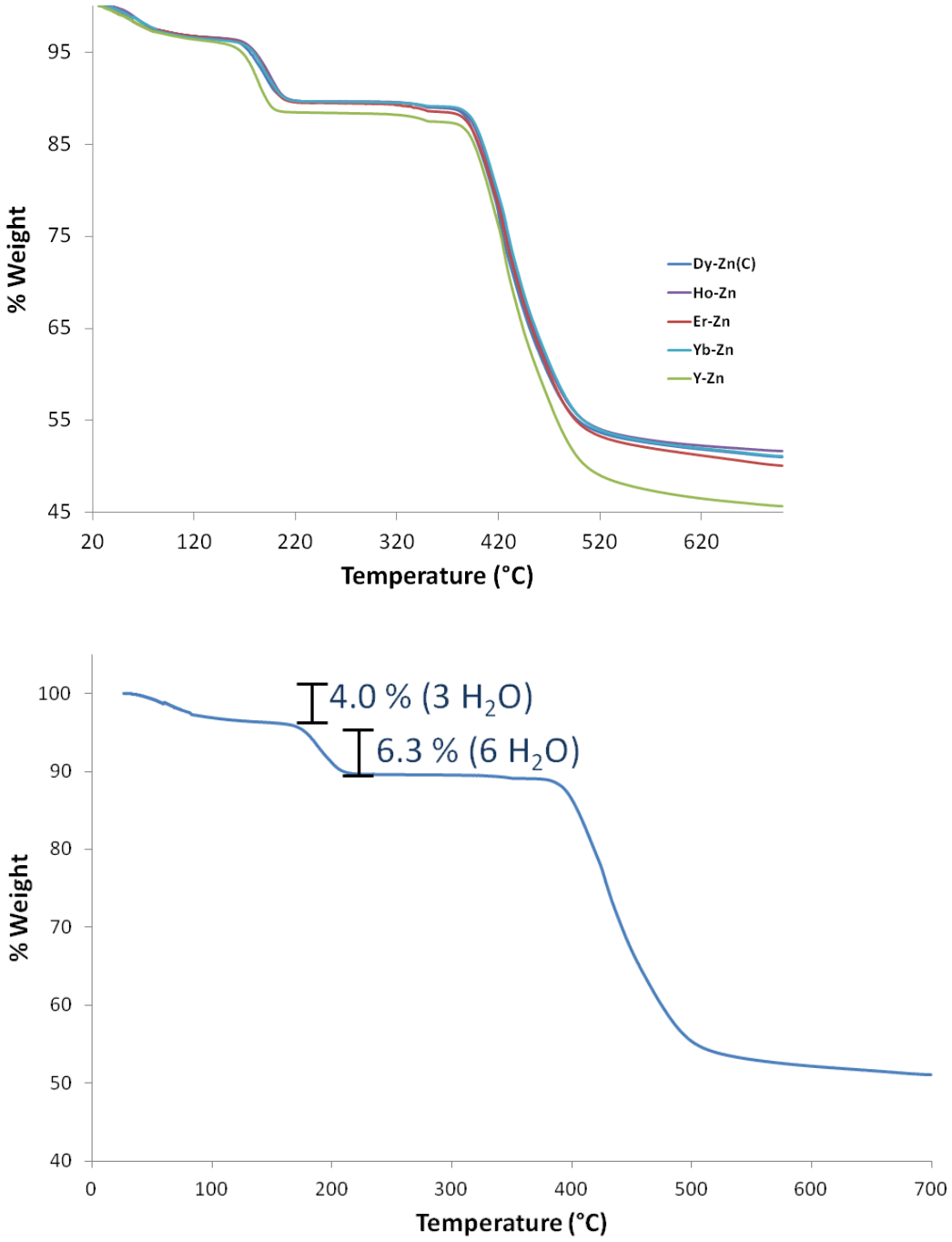


Figure S2. TGA curves for the **Ln-Zn** MOFs belonging to the cubic $Fd\bar{3}c$ space group. In detail the corresponding profile for $[\{Zn(H_2O)_6\}\{ZnYb(oda)_3\}_2]\cdot 3H_2O$

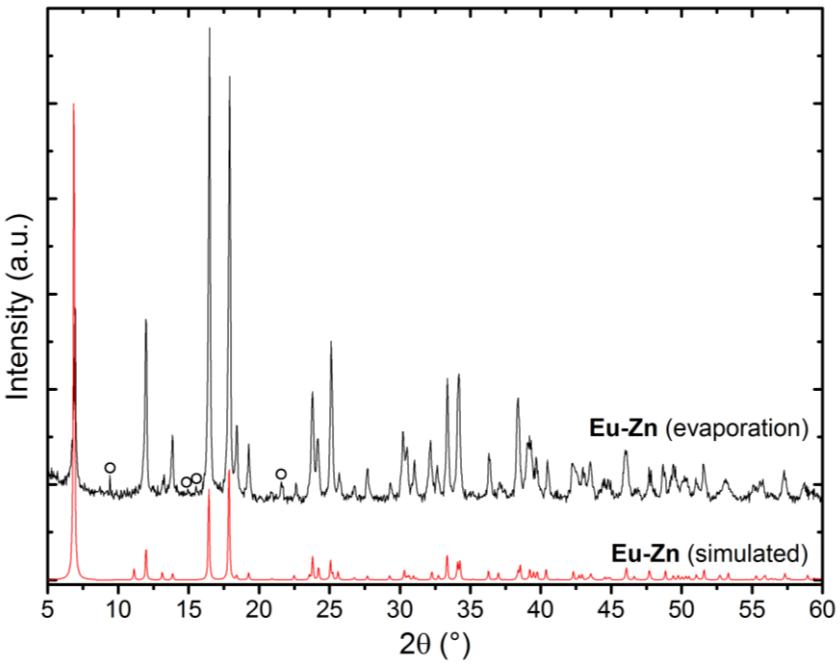


Figure S3. Powder diffraction pattern for **Eu-Zn** obtained by evaporation of the aqueous solution (black), and simulated from the adjusted structure (red). Impurity peaks are highlighted with a circle.

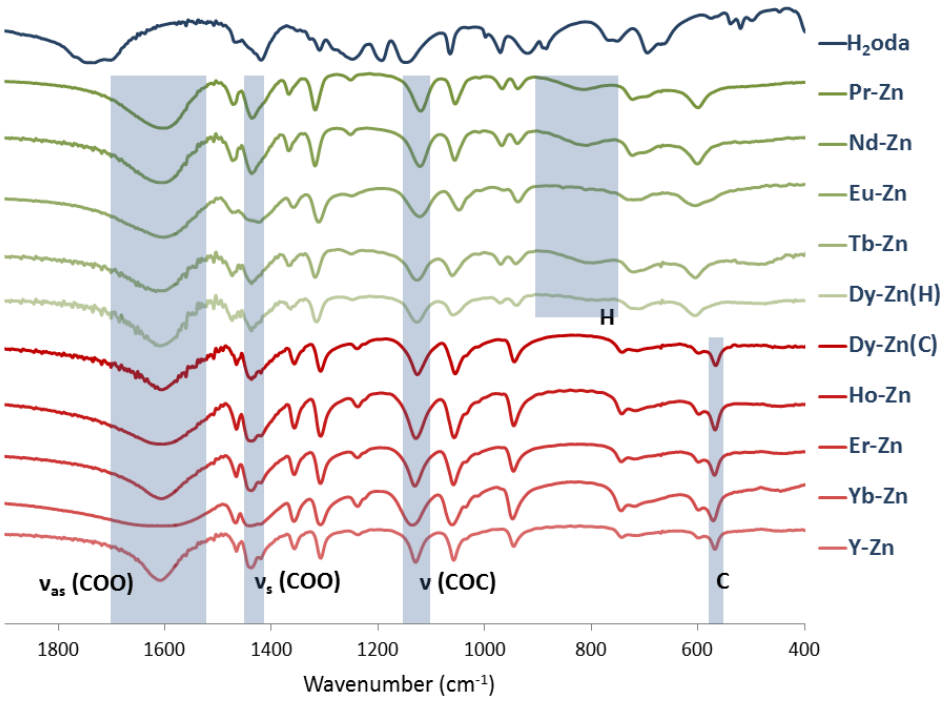


Figure S4. IR spectra for H_2oda and for the obtained **Ln-Zn** MOFs. Main band assignments are indicated as well as some characteristic bands that are identified for hexagonal (H) or cubic (C) forms.

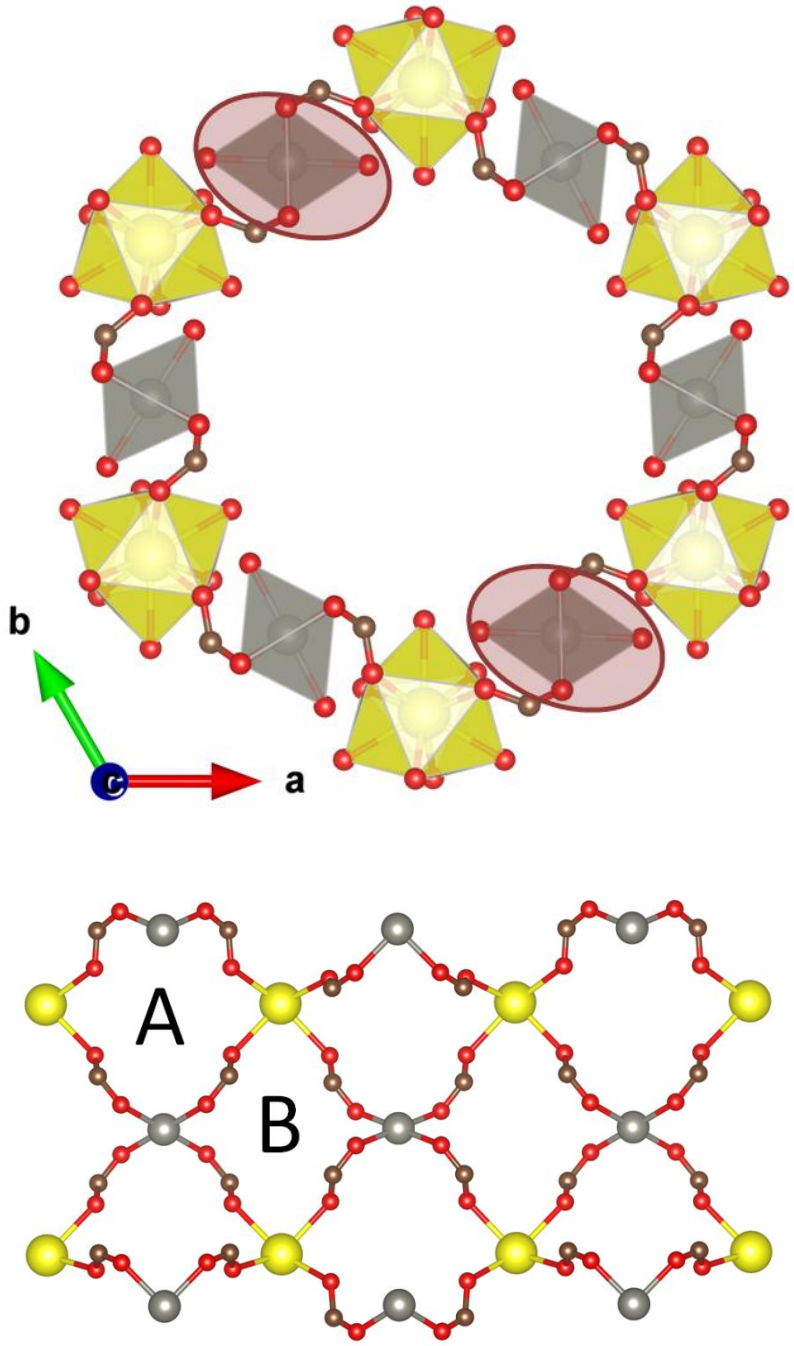


Figure S5. $Ln_2Zn_2(COO)_4$ and $Ln_6Zn_6(COO)_{12}$ SBUs in **Nd-Zn**.

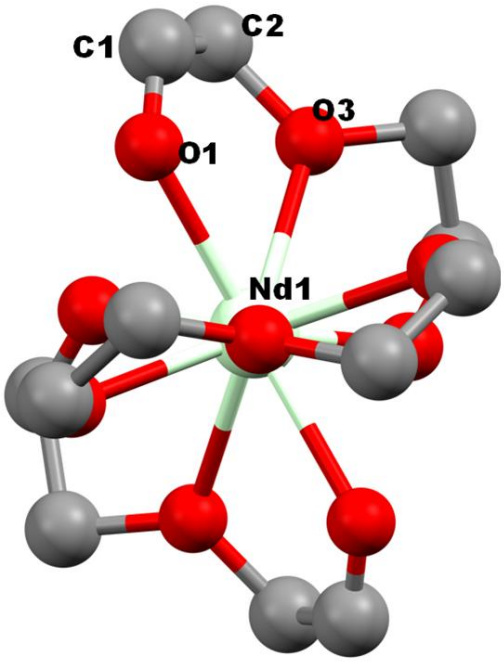


Figure S6. Connectivity around Nd for **Nd-Cd**.

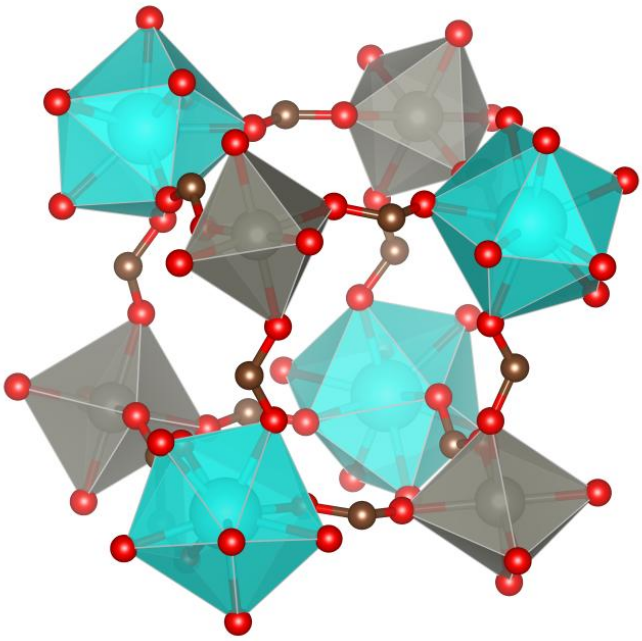


Figure S7. **Yb-Zn** secondary building unit.

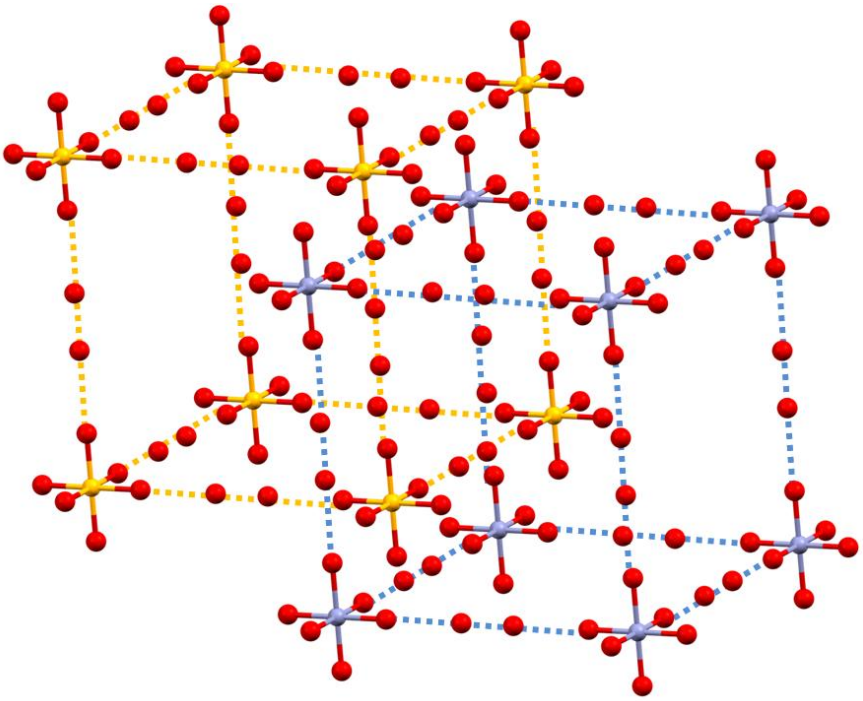


Figure S8. $[Zn(H_2O)]^{2+}$ interpenetrated structure in the **Yb-Zn** MOF.

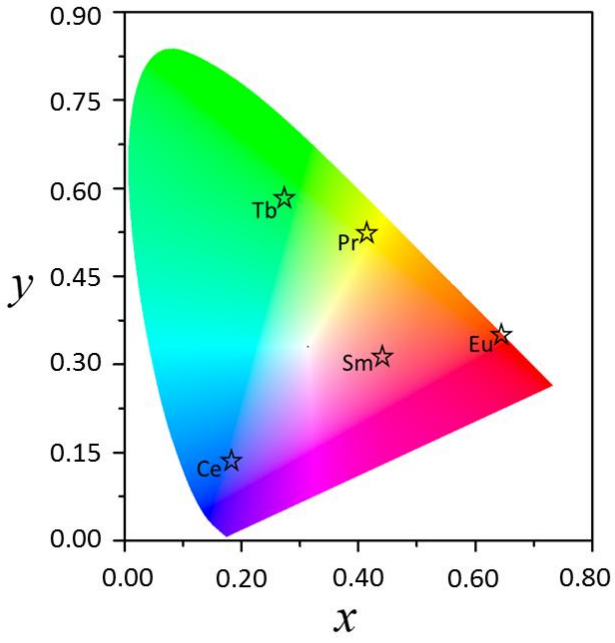
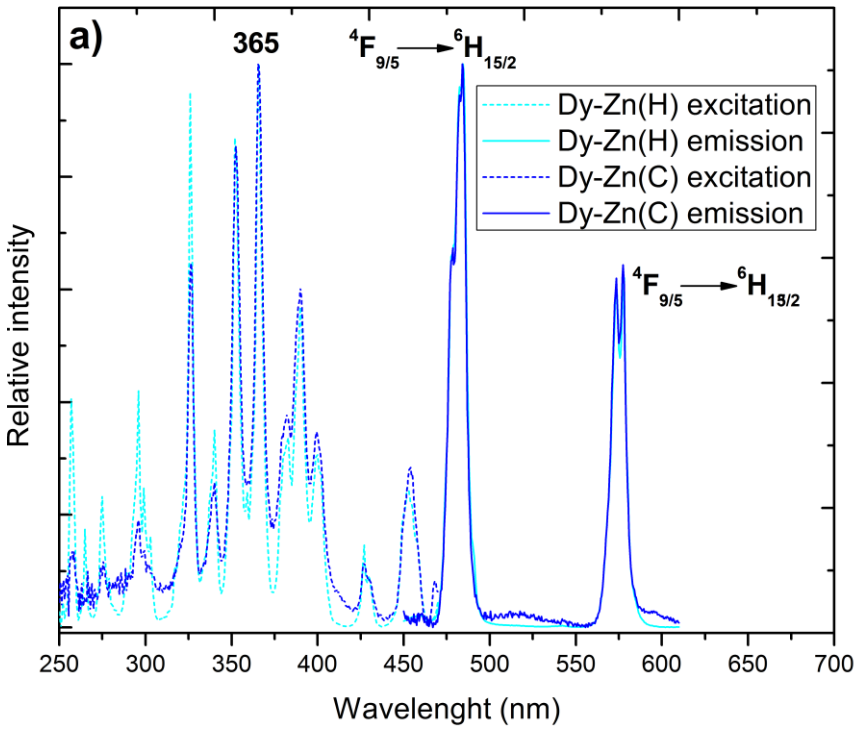


Figure S9. Color space chromaticity diagram with CIE coordinates for the emission of visible emitting Ln-Zn complexes at 298 K.



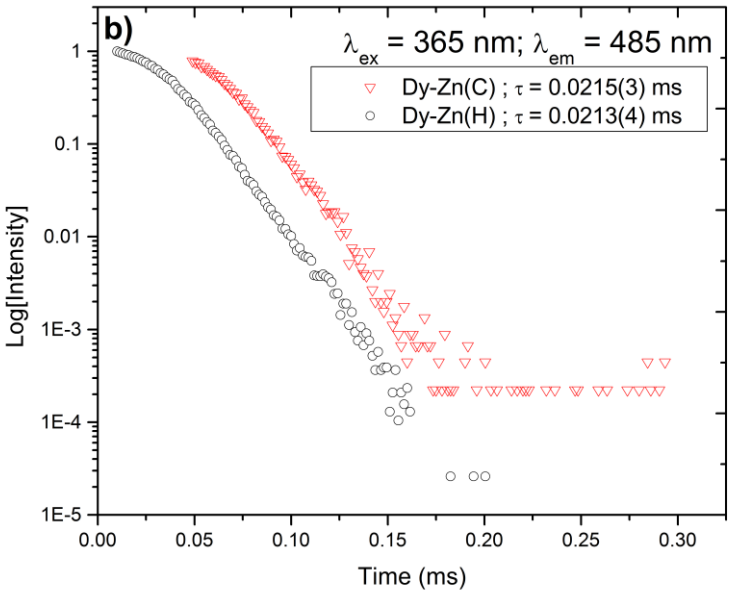


Figure S10. **Dy-Zn(H)** and **Dy-Zn(C)** luminescence studies. Excitation at 365nm. a)Emission spectra (continuous line) and the corresponding excitation spectra (dashed line). Time decay (τ) of **Dy-Zn(H)** and **Dy-Zn(C)** by monitoring the 485 nm emission; τ was determined by fitting a single exponential decay function of the form $I = I_0 e^{-\frac{t}{\tau}}$ in both cases.

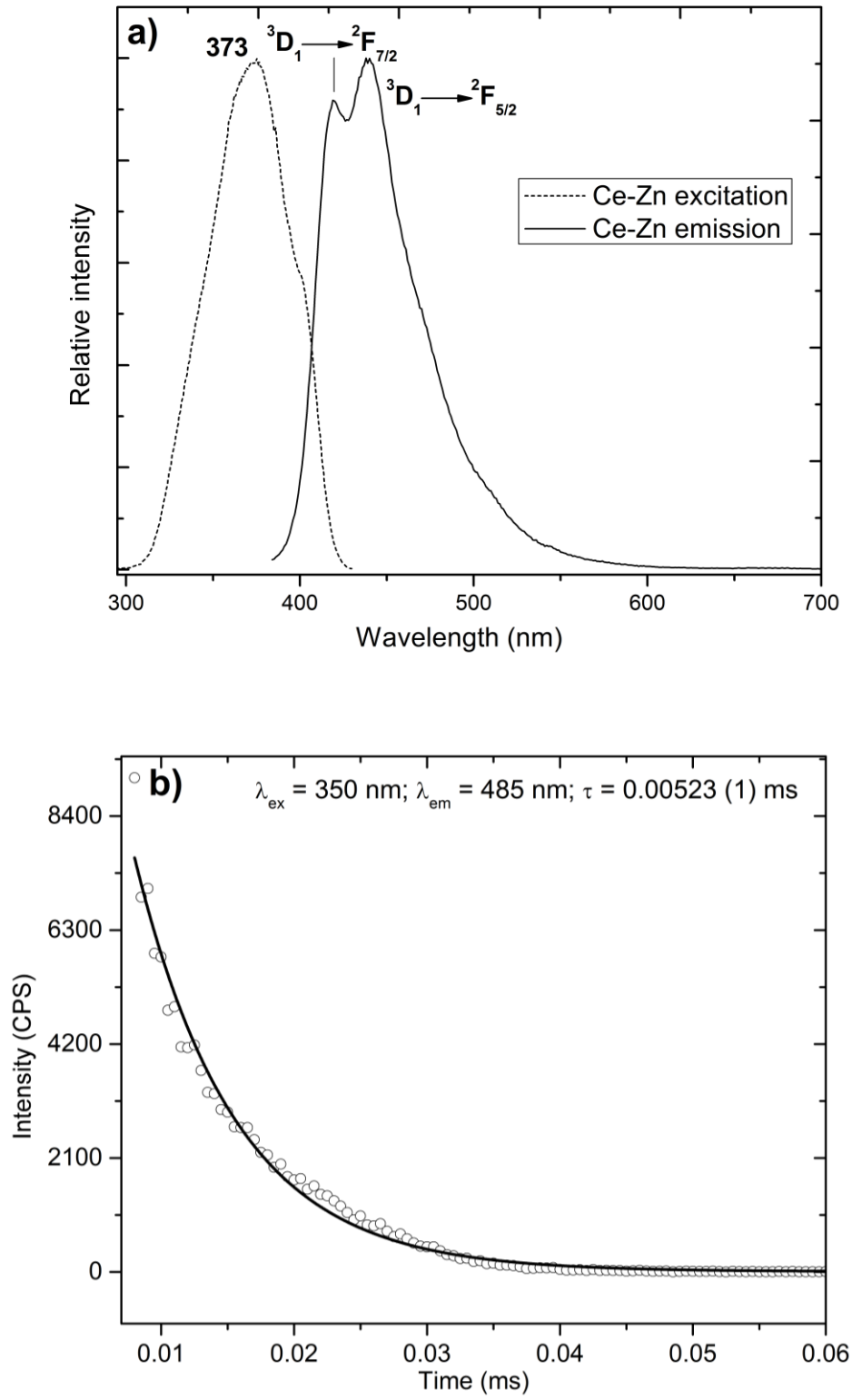


Figure S11. **Ce-Zn** luminescence studies. Excitation at 373 nm. a) Emission spectra (continuous line) and the corresponding excitation spectra (dashed line). b) Time decay (τ) monitoring the 485 nm emission; τ was determined by fitting a single exponential decay function of the form $I = I_0 e^{-\frac{t}{\tau}}$.

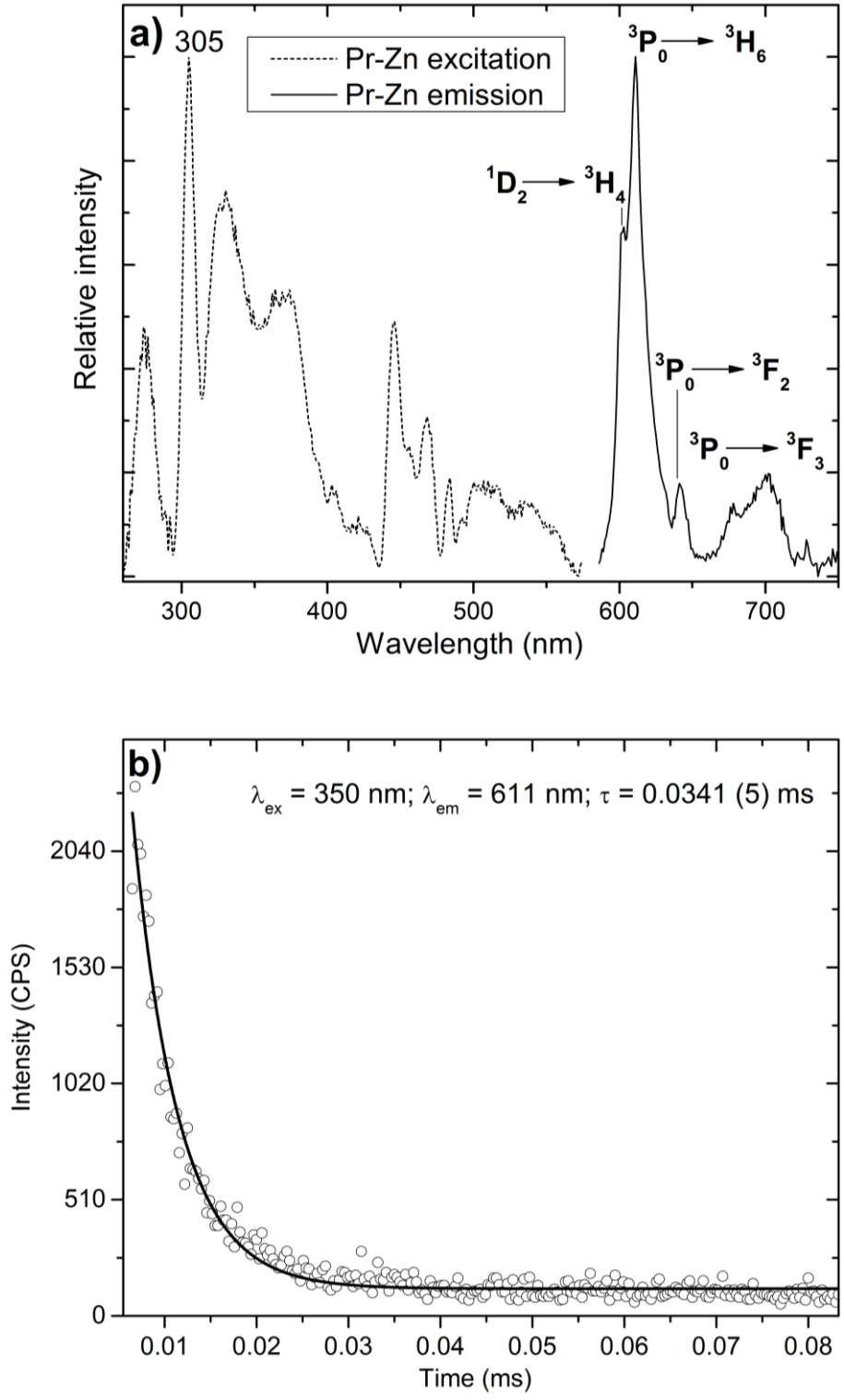


Figure S12. **Pr-Zn** luminescence studies. Excitation at 345 nm. a) Emission spectra (continuous line) and the corresponding excitation spectra (dashed line). b) Time decay (τ) monitoring the 611 nm emission; τ was determined by fitting a single exponential decay function of the form $I = I_0 e^{-\frac{t}{\tau}}$.

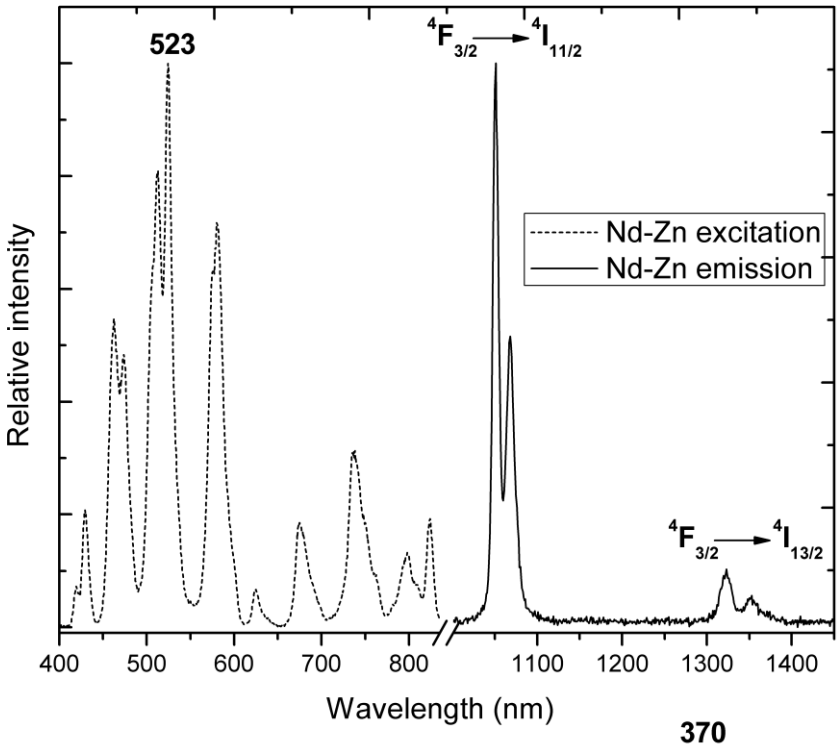


Figure S13. **Nd-Zn** luminescence studies. Excitation at 523 nm. Emission spectra (continuous line) and the corresponding excitation spectra (dashed line).

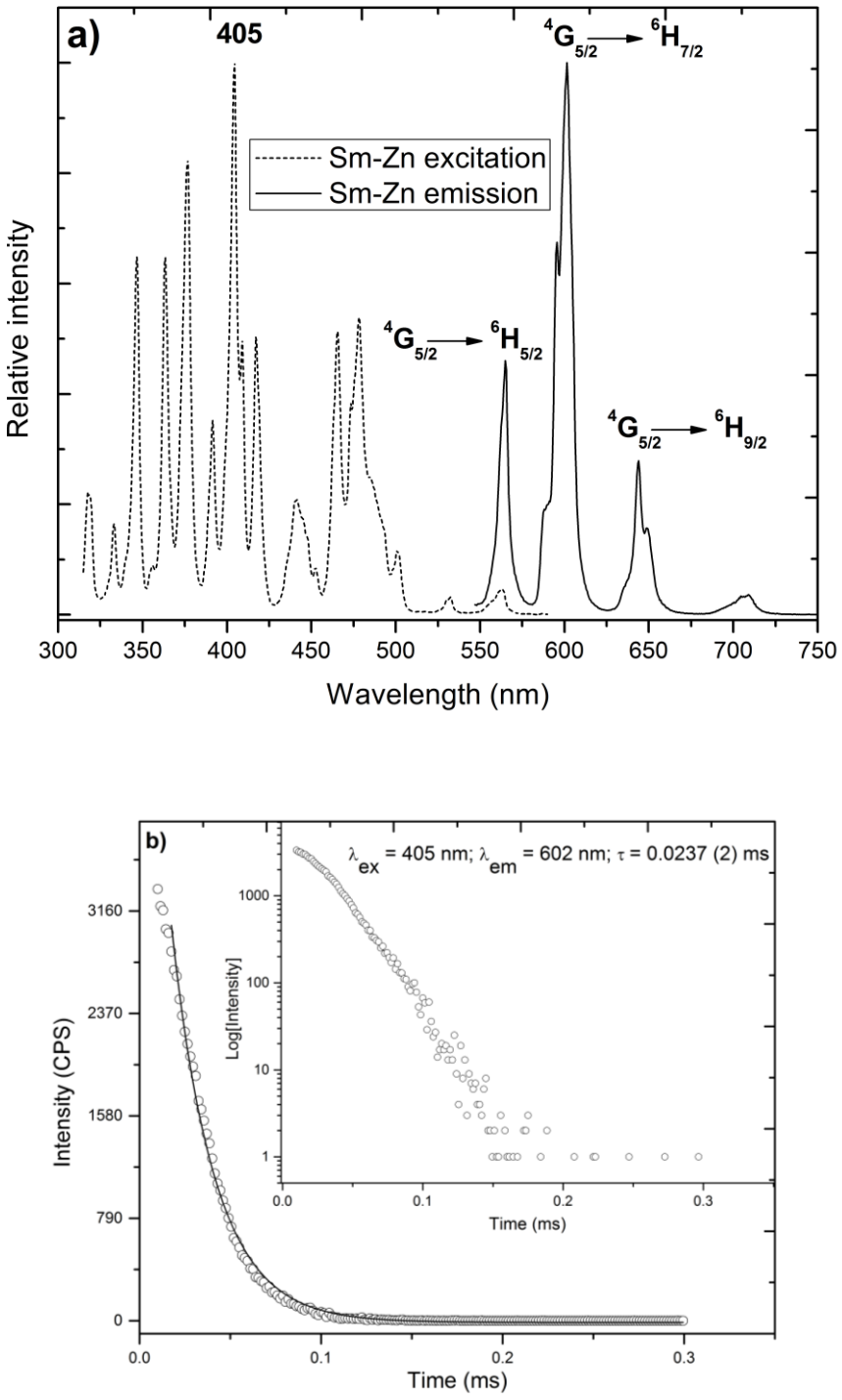


Figure S14. **Sm-Zn** luminescence studies. Excitation at 405 nm. a)Emission spectra (continuous line) and the corresponding excitation spectra (dashed line). b) Time decay (τ) monitoring the 602 nm emission; τ was determined by fitting a single exponential decay function of the form $I = I_0 e^{-\frac{t}{\tau}}$.

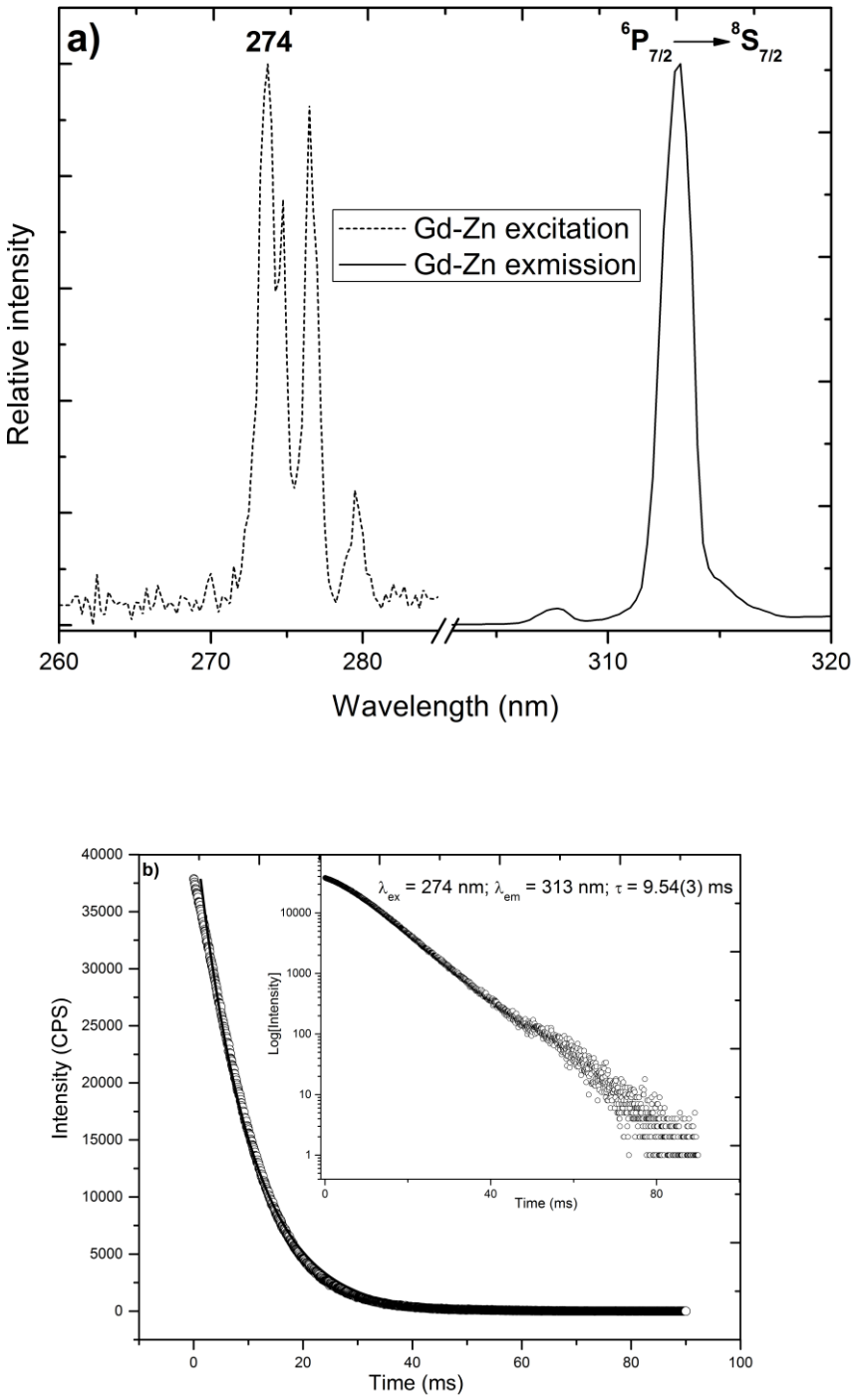


Figure S15. **Gd-Zn** luminescence studies. Excitation at 274 nm. a) Emission spectra (continuous line) and the corresponding excitation spectra (dashed line). b) Time decay (τ) when monitoring the 313 nm emission; τ was determined by fitting a single exponential decay function of the form $I = I_0 e^{-\frac{t}{\tau}}$.

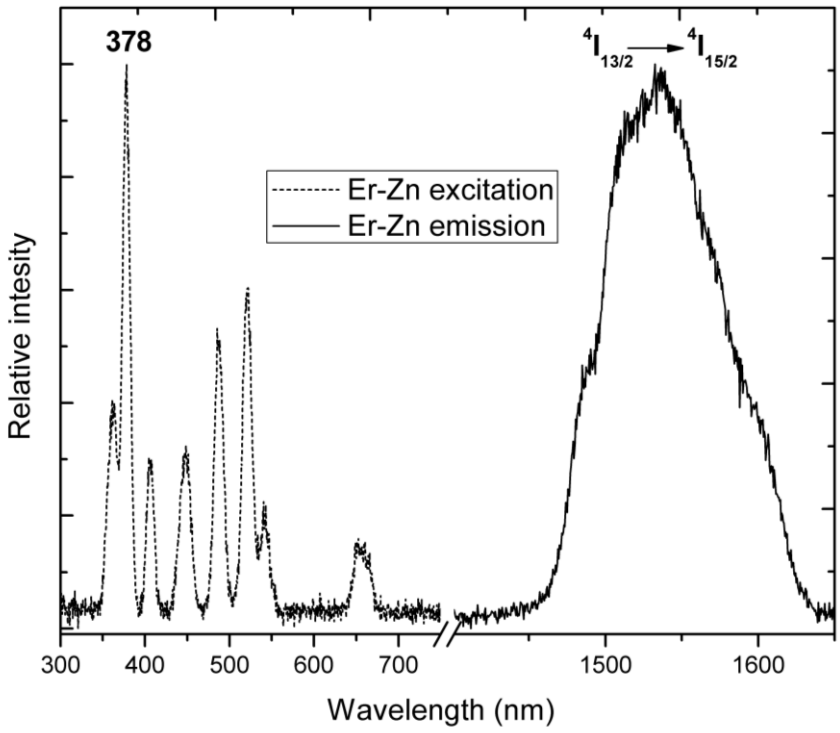


Figure S16. **Er-Zn** emission spectra excited with a 378 nm light (continuous line) and excitation spectra when monitoring the 1535 nm emission (dashed line).

Supplementary tables

Table S1. Continuous Shape Measure (CSHM) calculations for all new Ln-Zn synthesized compounds[2].

Ideal structure	Pr-Zn	Nd-Zn	Eu-Zn	Tb-Zn	Dy-Zn(H)	Dy-Zn(C)	Ho-Zn	Er-Zn	Yb-Zn	Y-Zn
Enneagon	31.75	32.46	34.09	33.95	34.57	34.32	34.30	34.36	34.39	34.31
Octagonal pyramid	25.11	24.74	24.00	24.06	23.76	23.92	23.91	23.87	23.83	23.92
Heptagonal bipyramid	17.61	17.84	18.43	18.46	18.69	18.96	19.04	19.10	19.24	18.95
Johnson triangular cupola	12.89	13.16	13.81	13.74	13.99	13.98	14.01	14.05	14.12	13.97
Capped cube	9.56	9.62	9.84	9.84	9.92	10.09	10.13	10.16	10.22	10.08
Spherical-relaxed caped cube	8.44	8.49	8.65	8.67	8.74	8.92	8.97	8.99	9.07	8.91
Capped square antiprism	3.04	2.92	2.68	2.64	2.56	2.42	2.39	2.37	2.32	2.42
Spherical capped square antiprism	2.15	2.02	1.72	1.71	1.63	1.46	1.43	1.41	1.36	1.47
Tricapped trigonal prism	2.18	2.14	2.10	2.01	1.99	1.80	1.76	1.75	1.69	1.80
Spherical tricapped trigonal prism	**1.80**	**1.61**	**1.19**	**1.19**	**1.06**	**0.95**	**0.92**	**0.90**	**0.85**	**0.96**
Tridiminished icosahedron	11.06	10.90	10.75	10.88	10.78	11.48	11.58	1.61	11.74	11.46
Hula-hoop	12.45	12.51	12.63	12.59	12.67	12.52	12.51	12.52	12.52	12.52
Muffin	2.71	2.60	2.34	2.33	2.26	2.11	2.09	2.07	2.04	2.12

*The CShM parameter is defined as a distance between the real and the ideal polyhedral.

Table S2 Excited state lifetimes for **Eu-Zn**.

	Ce-Zn	Pr-Zn	Sm-Zn	Eu-Zn	Gd-Zn	Tb-Zn	Dy-Zn(H)	Dy-Zn(C)
τ (ms)	0.00523(1)	0.0341(5)	0.0237(2)	2.141(7)	9.54(3)	3.79(2)	0.0213(4)	0.0215(3)

References

1 CIE-Datatables, *http://www.cie.co.at/publ/abst/datatables15_2004/z2.txt; http://www.cie.co.at/publ/abst/datatables15_2004/x2.txt; http://www.cie.co.at/publ/abst/datatables15_2004/y2.txt*.

2 P. Alemany, D. Casanova, S. Alvarez, C. Dryzun, M. Llunell and D. Avnir, *Rev. Comput. Chem.*