# Electronic Supplementary Information

## Multifunctional self-refrigerated multivariate {GdLn} (Ln = Dy, Tb, Tb/Eu) metal-organic frameworks

L. Zhen,[a,b] A. Arauzo,[c] C. Roscini,[d] J. Giner Planas[a]* and E. Bartolomé[a]*

[a] Institut de Ciència de Materials de Barcelona (ICMAB)-CSIC, Campus UAB, 08193-Bellaterra, Spain

[b] Shandong Provincial Key Laboratory of Monocrystalline Silicon Semiconductor Materials and Technology, College of Chemistry and Chemical Engineering, Dezhou University, Dezhou 253023, China

[c] Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, and Departamento de Física de la Materia Condensada, 50009 Zaragoza, Spain

[d] Catalan Institute of Nanoscience and Nanotechnology (ICN2) CSIC and Barcelona Institute of Science and Technology (BIST) Bellaterra, Barcelona 08193, Spain

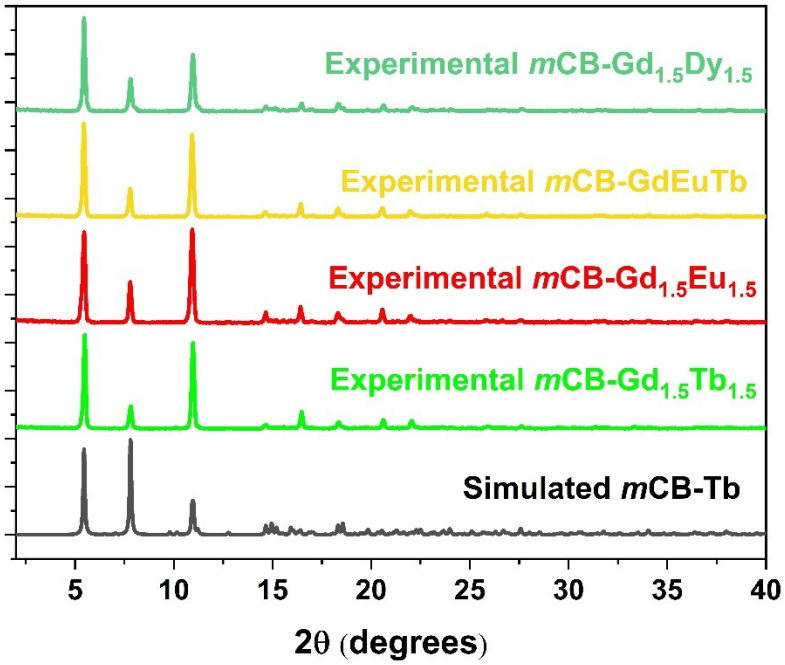


**Figure S1.** Comparison calculated (***m*CB-Tb**) and experimental (***m*CB-Gd$_{1.5}$Dy$_{1.5}$**, ***m*CB-GdEuTb,** ***m*CB-Gd$_{1.5}$Eu$_{1.5}$** and ***m*CB-Gd$_{1.5}$Tb$_{1.5}$**) PXRD patterns.

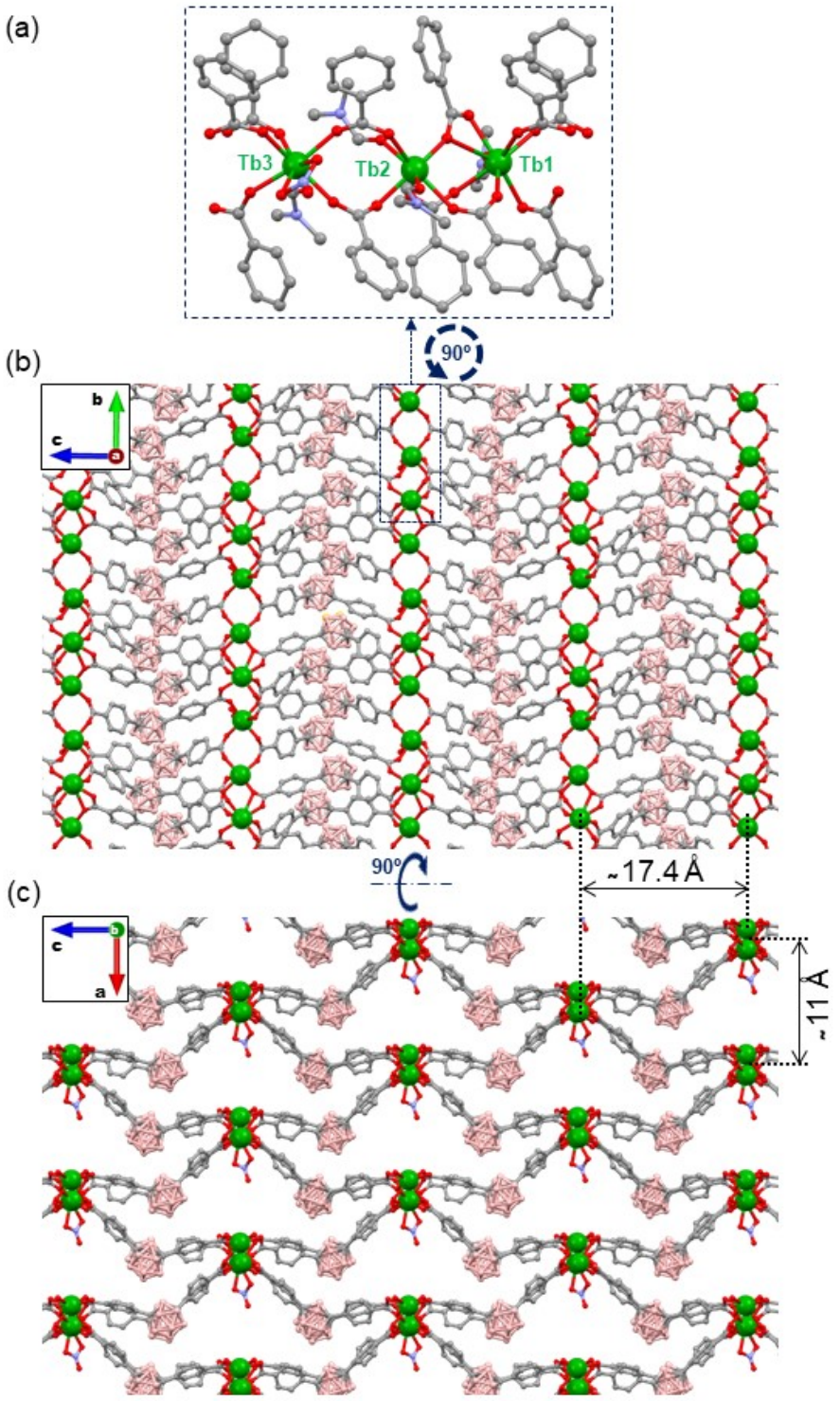


**Figure S2.** Structure of {[$(Tb)_3$(*m*CB-L)$_4$($NO_3$)$(DMF)_n$]·Solv}. (a) View of the coordination of *m*CB-L to the three independent Tb atoms that are repeated along the structure. (b,c) Two perpendicular views of the extended 3D framework, showing the 1-D Tb chains. Distances between the polymeric 1D Tb chains are indicated. Colour code: Tb (green), O (red), B (orange), C (grey); N (blue); H atoms (a-c) and DMF molecules (b-c) are omitted for clarity.

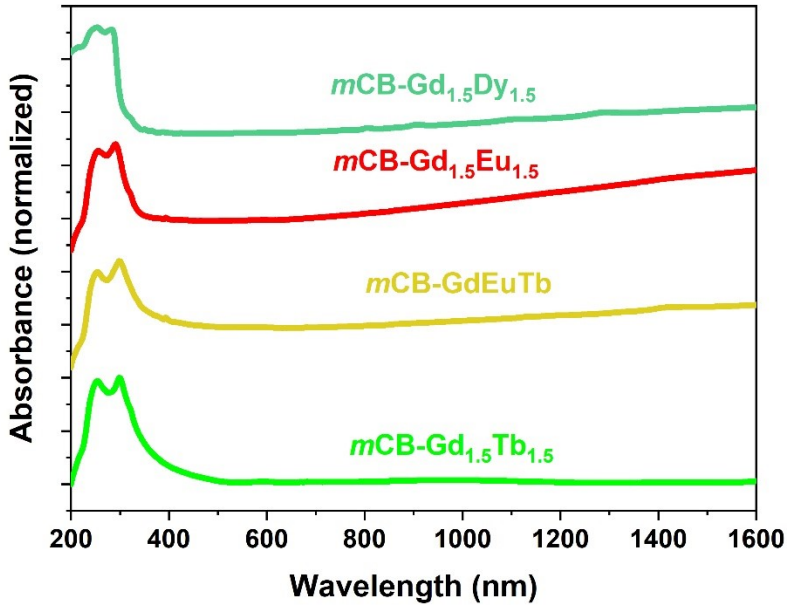


**Figure S3.** Solid state UV-vis spectra for **$Gd_{1.5}Dy_{1.5}$** (a), **$Gd_{1.5}Tb_{1.5}$** (b), **$Gd_{1.5}Eu_{1.5}$**(c) and **GdEuTb** MOFs.

**Table S1.** Orbital ($m_L$), spin ($m_s$) and total magnetic moment ($m_{TOT} = m_L + m_s$) for each ion in the mixed {GdLn} MOFs determined from the XAS-XMCD spectra at 3.4 K and 6 T using the corrected sum rules for lanthanides.[1,2]

| **MOF** | **Ln** | **$n_h$** | **$m_L$/ion ($\mu_B$)** | **$m_s$/ion ($\mu_B$)** | **$m_{TOT}$/ion ($\mu_B$)** |
|---|---|---|---|---|---|
| **$Gd_{1.5}Dy_{1.5}$** | $Gd^{3+}$ | 7 | 0.36 | 6.37 | 6.72 |
| | $Dy^{3+}$ | 5 | 2.51 | 2.34 | 4.85 |
| **$Gd_{1.5}Tb_{1.5}$** | $Gd^{3+}$ | 7 | 0.37 | 6.31 | 6.68 |
| | $Tb^{3+}$ | 6 | 1.59 | 2.73 | 4.32 |
| **$Gd_{1.5}Eu_{1.5}$** | $Gd^{3+}$ | 7 | 0.35 | 6.39 | 6.74 |
| | Eu ($Eu^{2+}/Eu^{3+}$=0.24/0.76) | 7.76 | -0.06 | 2.11 | 2.05 |
| **GdEuTb** | $Gd^{3+}$ | 7 | 0.30 | 6.32 | 6.62 |
| | Eu ($Eu^{2+}/Eu^{3+}$=0.26/0.74) | 7.73 | 0.01 | 2.11 | 2.12 |
| | $Tb^{3+}$ | 6 | 1.39 | 2.95 | 4.34 |

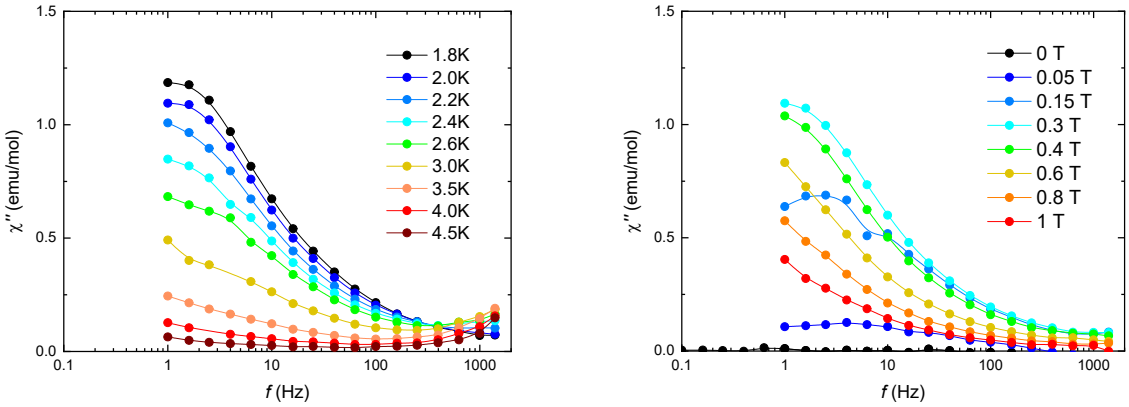


**Figure S4. Spin magnetic relaxation of mixed {GdEuTb} MOF.** Left: imaginary component of the ac susceptibility as a function of the frequency, $\chi''(f)$, at $\mu_0 H$=0.3 T, and Right: at $T$=2 K and different applied magnetic fields.

**Table S2**. Comparison of solid state fluorescence parameters for mixed {GdLn} MOFs.

| MOF | $\lambda_{em}$ (nm) | Φ (%) | τ (μs) |
|---|---|---|---|
| $Gd_{1.5}Dy_{1.5}$ | 480, 572, 665 | 0.2 | 37.3 |
| $Gd_{1.5}Tb_{1.5}$ | 488, 542, 582, 619 | 7.3 | 872.5 |
| $Gd_{1.5}Eu_{1.5}$ | 543, 591, 614, 652, 699 | 4.2 | 739.1 |
| GdEuTb | 488, 541, 591, 614, 652, 699 | 4.5 | 867.1 for $Tb^{3+}$<br>744.1 for $Eu^{3+}$ |

$\lambda_{exc} = 280$ nm.

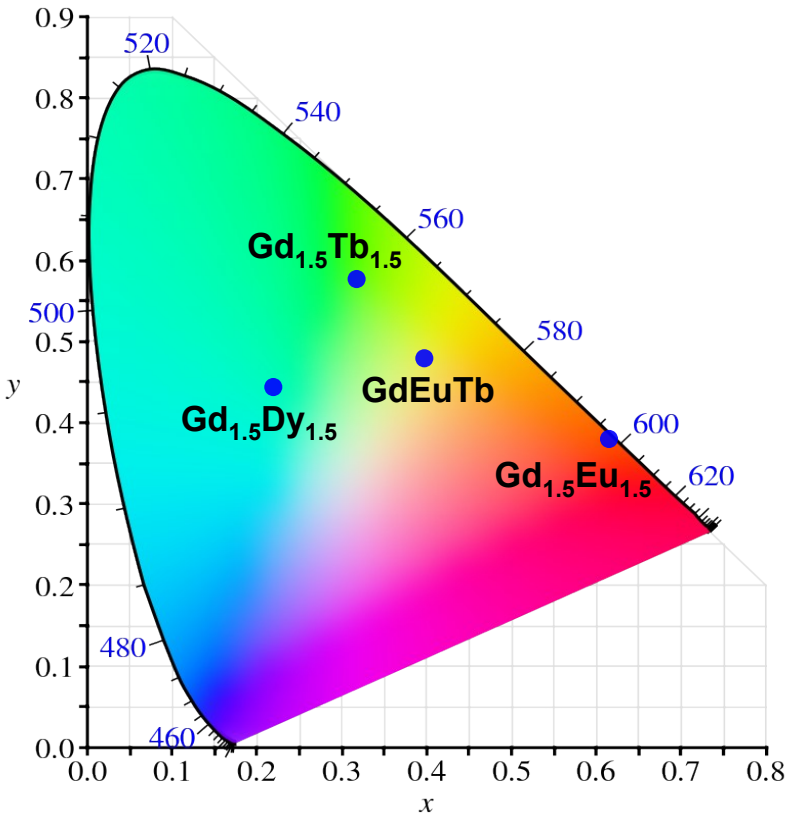


**Figure S5.** Color coordinates drawn onto the 1931 CIE chromaticity diagram for **$Gd_{1.5}Dy_{1.5}$**, **$Gd_{1.5}Tb_{1.5}$** and **$Gd_{1.5}Eu_{1.5}$** and **GdEuTb**.

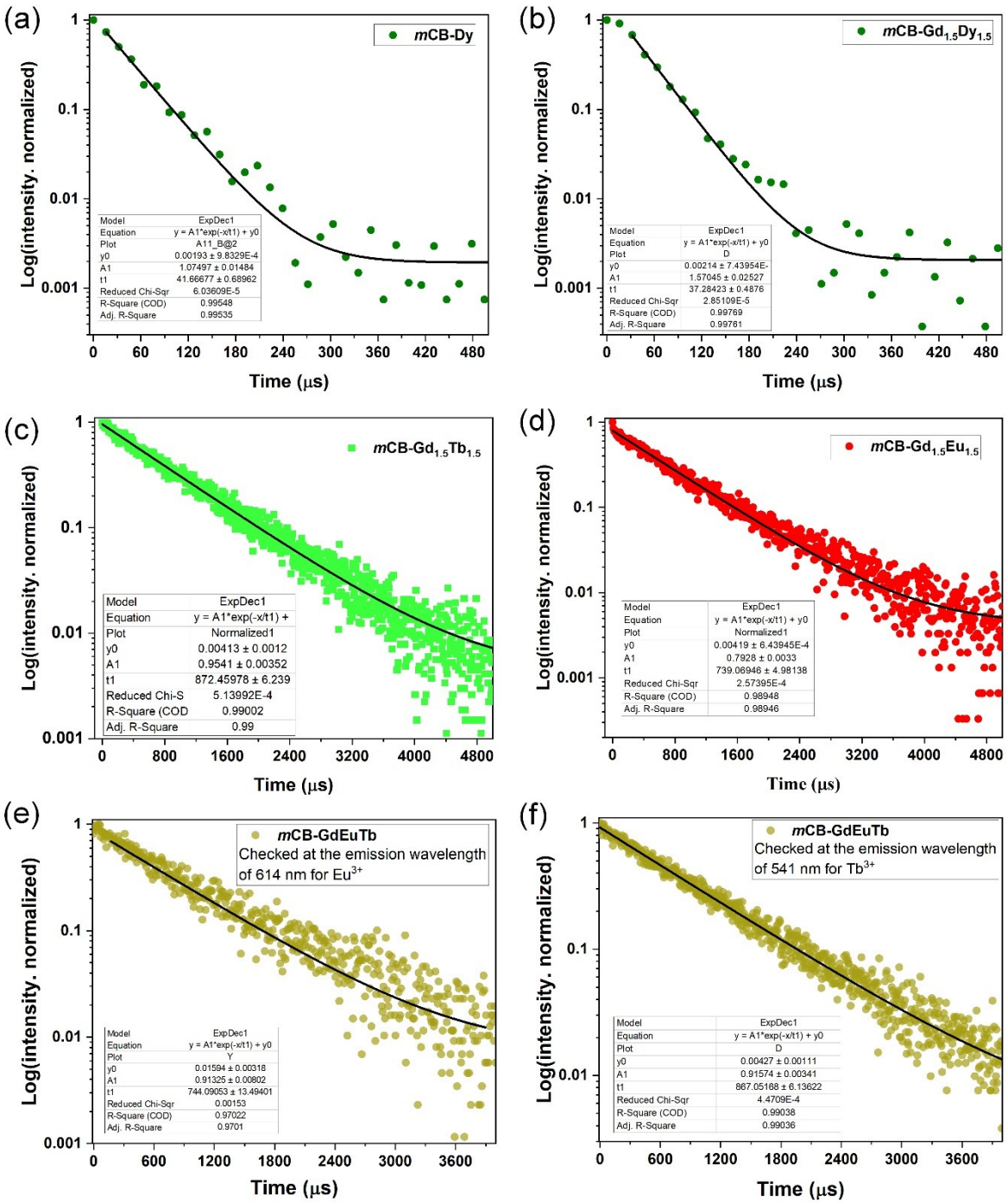


**Figure S6.** Luminescence decays of *m*CB-Dy (a), *m*CB-**$Gd_{1.5}Dy_{1.5}$** (b), *m*CB-**$Gd_{1.5}Tb_{1.5}$** (c), *m*CB-**$Gd_{1.5}Eu_{1.5}$**(d) and *m*CB-**GdEuTb** (e and f) under continuous-wave irradiation ($\lambda_{exc}$ = 280 nm) at room temperature.

## References


1 S. Tripathi, Max-Planck-Institut für Intelligente Systeme, Stuttgart, 2018.

2 B. Thole, P. Carra, F. Sette and G. van der Laan, *Phys. Rev. Lett.*, 1992, **68**, 1943–1946.