

## Supporting Information

### Design of lanthanide-based metal-organic frameworks with enhanced near-infrared emission

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## 1. General information

All chemicals were purchased from commercial vendors and used without further purification. The carboxylic acid H<sub>3</sub>tctb was synthesized based on the previously reported procedure.<sup>1</sup> All reactions were carried out under aerobic conditions, unless otherwise stated. Single crystal X-ray diffraction data were collected using a Bruker D8 Venture four-circle diffractometer equipped with a MoK $\alpha$  microfocus sealed X-ray tube and a Photon 100 2D CMOS detector. PXRD data were collected on a Bruker D8 Advance using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ , 50 kW/40mA) operating in the Bragg-Brentano geometry. Prior to measurements, the crystals were finely ground and deposited on a silicon wafer zero-background sample holder. The PXRD pattern was indexed ab initio using a dichotomy method with the DICVOL06 program,<sup>2</sup> while the Le Bail refinement was performed using the FullProf program suite.<sup>3</sup> Simulated powder X-ray diffraction patterns were generated from the single crystal data using Mercury 3.7. Topologies of the MOFs were calculated by the program ToposPro v.5.0.0.0. Elemental analyses were performed on a FLASH 2000 elemental analyzer (Thermo Scientific). Thermogravimetric analysis (TGA) was performed in air on a TGA 8000 instrument with a heating rate of 5 °C/min. Infrared spectra were collected on a Spectrum Two FTIR Spectrometer (PerkinElmer) from 400 to 4000 cm<sup>-1</sup>. UV/vis absorption spectra were obtained with a Lambda 950S PerkinElmer UV/vis Spectrometer. Scanning electron microscopy (SEM) images were obtained from a FEI Teneo instrument equipped with an energy dispersive X-ray (EDX) detector (XFlash Silicon drift detector).

## 2. Synthesis

All the MOFs were synthesized using the Biotage microwave synthesizer.

**HL1-Ln** (Ln = Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb) (or **HL1-Y**): 0.025 mmol of Ln(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O (or Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O) and 0.025 mmol of H<sub>3</sub>tctb (13.50 mg) were dissolved in 2.0 mL of DMF, to which 1.0 mL of H<sub>2</sub>O was added. The clear solution mixture was then transferred to a 12 mL microwave vial, sealed, and heated under microwave irradiation (power = 200 W) for 40 mins at 180 °C. Single crystals of **HL1-Ln** (or **HL1-Y**) were formed, filtered, washed with DMF and dried in air. Yield: ~ 10 – 12 mg.

**HL1-Ln/Y** (Ln = Ho, Er, Yb): 0.0125 mmol of Ln(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O, 4.79 mg (0.0125 mmol) of Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, and 13.50 mg (0.025 mmol) of H<sub>3</sub>tctb were dissolved in 2.0 mL of DMF, to which 1.0 mL of H<sub>2</sub>O was added. The clear solution mixture was then transferred to a 12 mL microwave vial, sealed, and heated under microwave irradiation (power = 200 W) for 40 mins at 180 °C. Crystals of **HL1-Ln/Y** were formed, filtered, washed with DMF and dried in air. Yield: ~ 10 mg.

## 3. Single-crystal X-ray diffraction

### 3.1 Crystal structure

Single crystals of **HL1-Eu** were isolated from the reaction mixture. A suitable crystal was selected and mounted onto a BRUKER D8 VENTURE four-circle diffractometer equipped with a MoK $\alpha$  microfocus sealed X-ray tube and a Photon 100 2D CMOS detector. The crystal was kept at 100 K during data collection. The crystal structure was solved with SHELXT<sup>4</sup> and refined with SHELXL<sup>5</sup> programs integrated within the Olex2 program suite.<sup>6</sup> Reflection 010 was found to be affected by the beamstop, and hence it was omitted from the refinement. All non-H atoms were

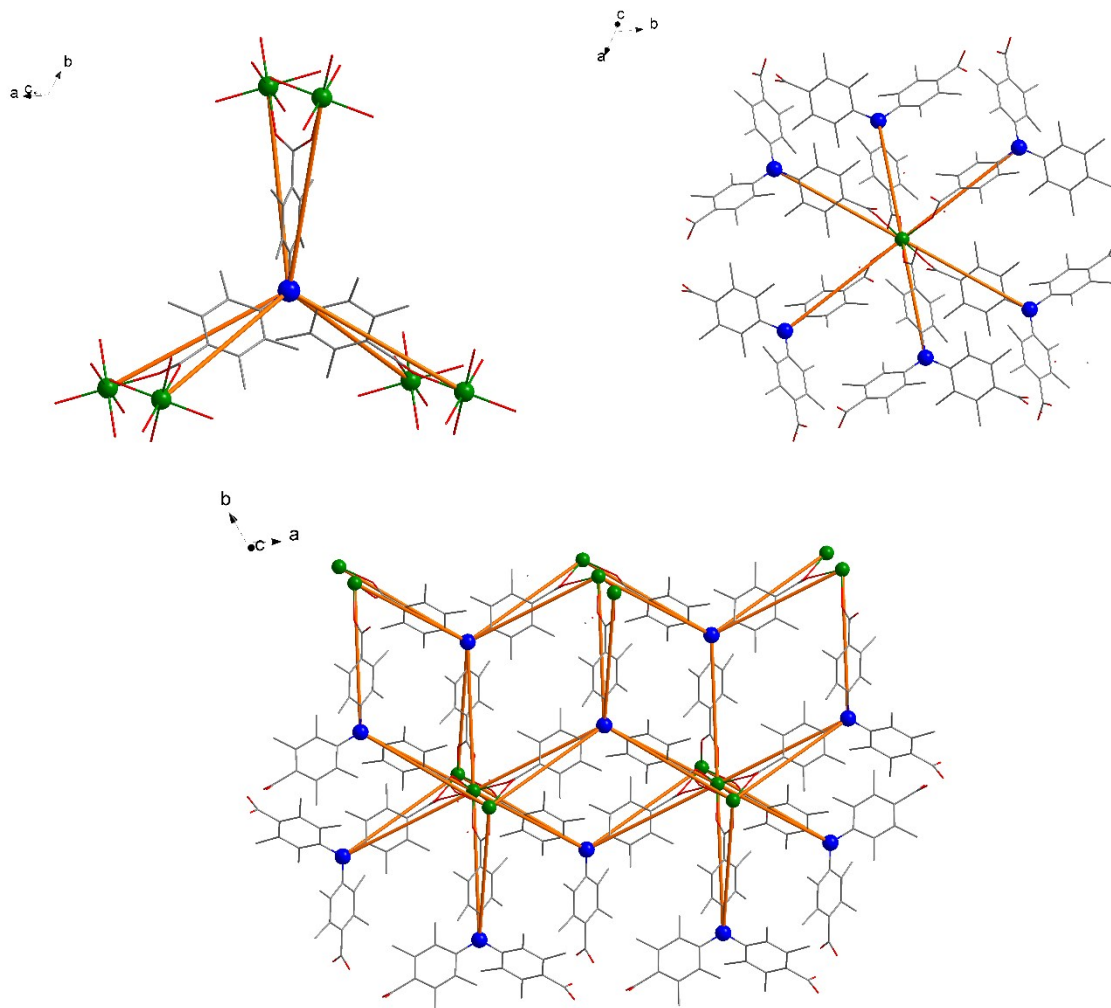
found upon solution and refined anisotropically. Aliphatic H atoms were introduced based on the molecular geometry and electron density map as an idealised rotating CH<sub>3</sub> group using the AFIX 137 command. The planarity of the phenyl ring was assured with the FLAT command with the low standard uncertainty. The atomic displacement parameters of all C atoms belonging to the tctb<sup>3-</sup> ligand were restrained with the RIGU command. The contribution of the disordered solvent molecules found in the structural voids to the measured structure factors was quantified using the solvent masking procedure implemented in Olex2 equivalent to PLATON SQUEEZE.<sup>6-8</sup> There are two voids per each unit cell; each void has a volume of 169.6 Å<sup>3</sup> and accounts for 26.8 e<sup>-</sup>. The identity and geometry of chemical species residing inside the pores could not be determined with the diffractometric methods. CCDC 1946819.

Table S1. Crystal data and structure refinement for **HL1-Eu**.

Identification code	<b>HL1-Eu</b>
Empirical formula	C <sub>33</sub> H <sub>36</sub> BEuO <sub>6</sub>
Formula weight	691.37
Temperature/K	99.95
Crystal system	trigonal
Space group	P-31c
a/Å	14.5046(9)
b/Å	14.5046(9)
c/Å	9.2626(6)
α/°	90
β/°	90
γ/°	120
Volume/Å <sup>3</sup>	1687.6(2)
Z	2.00004
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.361
μ/mm <sup>-1</sup>	1.897
F(000)	700.0
Crystal size/mm <sup>3</sup>	0.06 × 0.06 × 0.025
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.464 to 50.044
Index ranges	-16 ≤ h ≤ 17, -17 ≤ k ≤ 17, -11 ≤ l ≤ 11
Reflections collected	12798
Independent reflections	1005 [R <sub>int</sub> = 0.1077, R <sub>sigma</sub> = 0.0423]
Data/restraints/parameters	1005/66/67
Goodness-of-fit on F <sup>2</sup>	1.044
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0391, wR <sub>2</sub> = 0.1007
Final R indexes [all data]	R <sub>1</sub> = 0.0611, wR <sub>2</sub> = 0.1108
Largest diff. peak/hole / e Å <sup>-3</sup>	1.11/-0.44

### 3.2 Structural topology

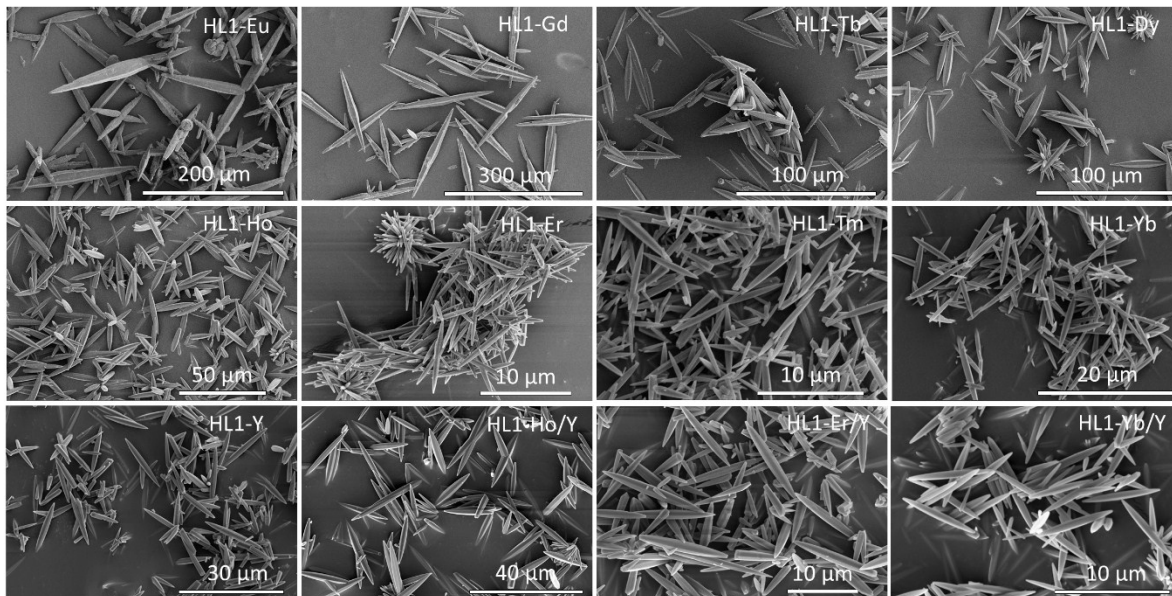
**HL1-Eu** forms a 2-nodal net which is described with the Schläfli symbol  $(4^{12}.6^3)(4^9.6^6)$  and the three-letter code *nia* (NiAs-type).<sup>9</sup> The 6-coordinated node A is associated with the  $tctb^{3-}$  ligand (Fig. S1, top left), while the 6-coordinated node B is associated with the Eu atom (Fig. S1, top right). The connectivity of the net reflects the actual array of the coordination bonds (each  $tctb^{3-}$  is coordinated to 6 Eu atoms, while each Eu atom coordinates 6  $tctb^{3-}$  ligands). Stoichiometry of the net amounts to AB.



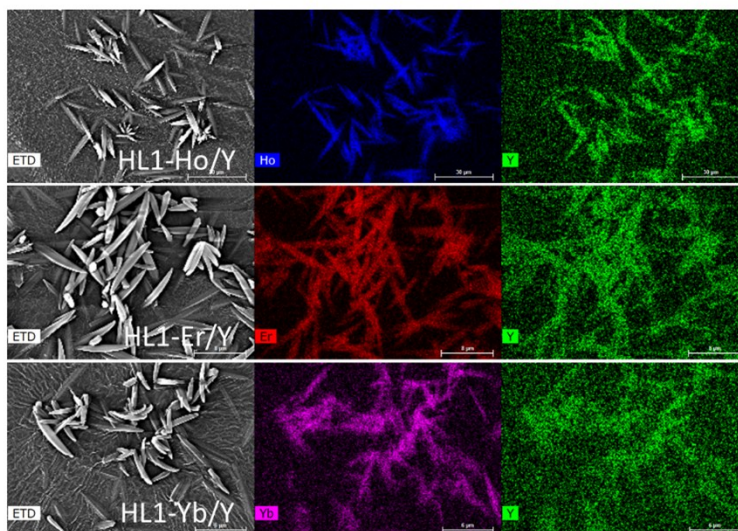
**Figure S1.** (top left)  $tctb^{3-}$  ligand situated at  $2/3, 1/3, 1/4$ , acting as a 6-c node *A* of the underlying *nia* net; (top right) Atom Eu1 situated at  $0, 0, 1/2$ , acting as a 6-c node *B* of the underlying *nia* net; (bottom) Topological description of **HL1-Eu** as the 2-nodal *nia* net (NiAs-type, Schläfli symbol  $(4^{12}.6^3)(4^9.6^6)$ ) composed of the nodes *A* and *B* with the *AB* stoichiometry. Thin two-coloured lines refer to the chemical bond, whereas thick orange lines – to the links of the underlying net. Colour code: C, grey; O, red; B = node *A*, blue; Eu = node *B*, green. H atoms are omitted for clarity.

#### 4. Characterization

##### 4.1 Scanning electron microscopy and Energy dispersive X-ray spectroscopy



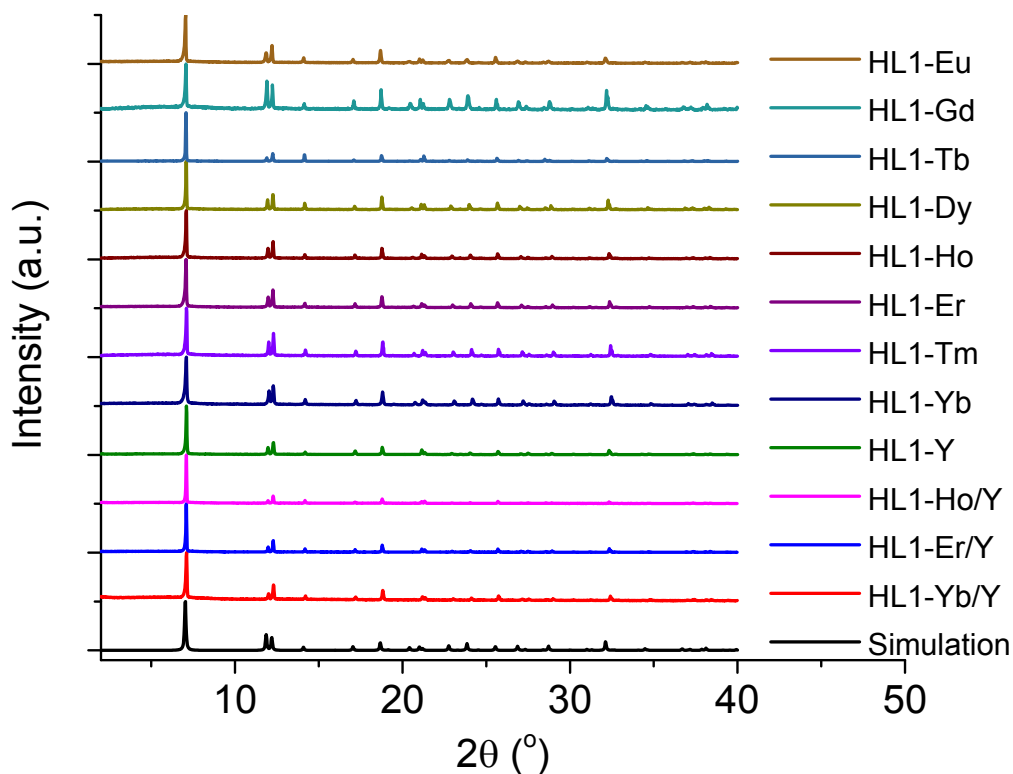
**Figure S2.** SEM images of **HL1-Ln**, **HL1-Y** and **HL1-Ln/Y** MOFs.



**Figure S3.** EDX mapping image of **HL1-Ho/Y**, **HL1-Er/Y**, and **HL1-Yb/Y**.

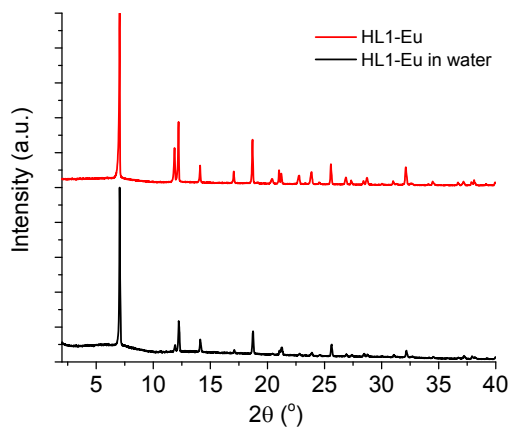


## 4.2 Powder X-ray diffraction

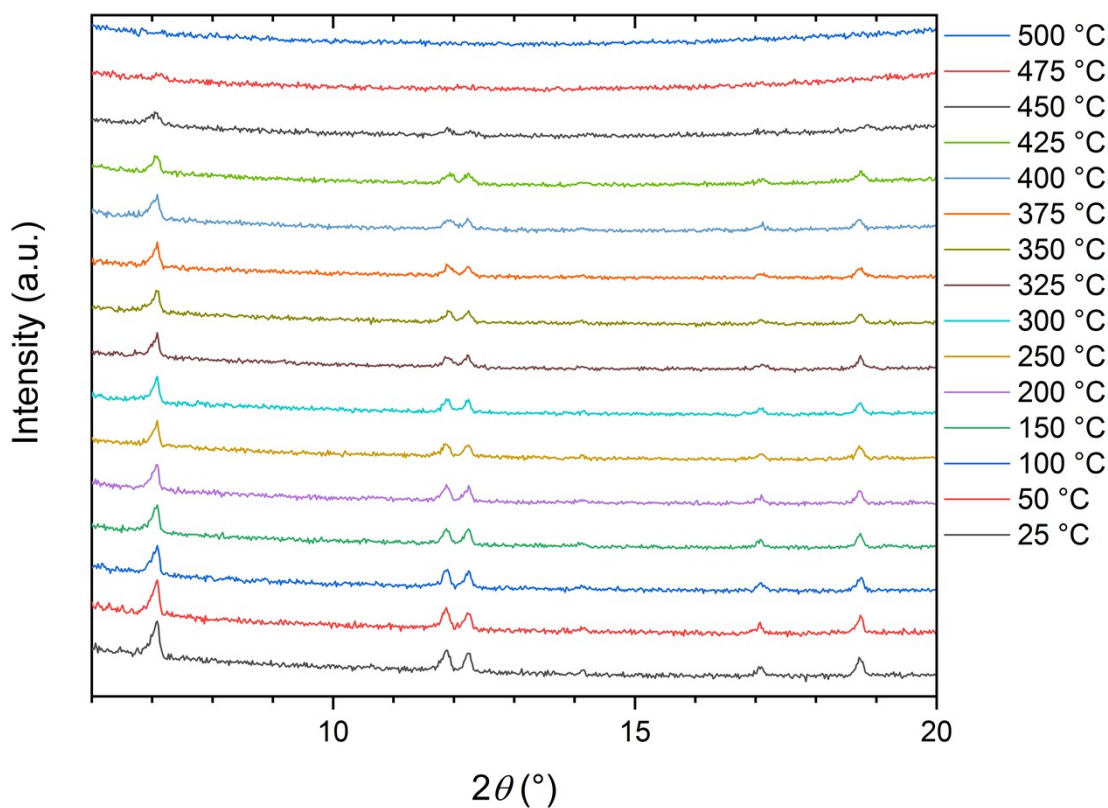


**Figure S4.** PXRD patterns of **HL1-Ln**, **HL1-Y**, and **HL1-Ln/Y** MOFs.

To investigate the water stability of **HL1-Eu**, the powder sample was submerged in deionized water for 24 hours, filtered, and dried in air before measuring the PXRD pattern.



**Figure S5.** PXRD patterns of **HL1-Eu** immersed in water for 24 hr, confirming the hydrolytic stability of the MOF.



**Figure S6.** Variable temperature PXRD pattern of **HL1-Eu**, demonstrating its thermal stability up to  $\sim 400$  °C.

#### 4.3 Elemental analysis and ICP-OES

##### **Elemental analysis for HL1-Eu ([Eu(tctb)])**

Calculated for  $C_{33}H_{36}BEuO_6$

C 57.33; H 5.25; N 0.00

Found

C 57.28; H 5.26; N 0.00

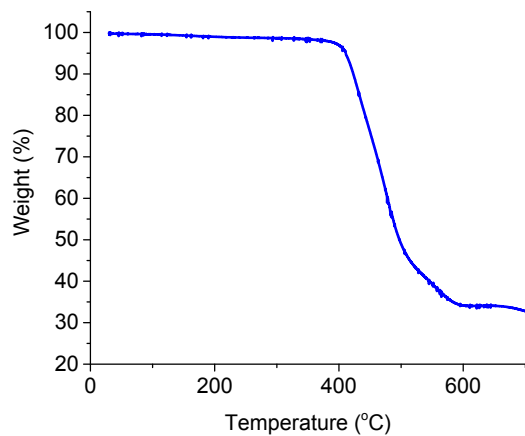
##### **ICP-OES**

2.30 mg of **HL1-Eu** was dissolved in 10.0 ml  $HNO_3$  solution.

Calculated concentrations of  $Eu^{3+}$ : 50.55 ppm

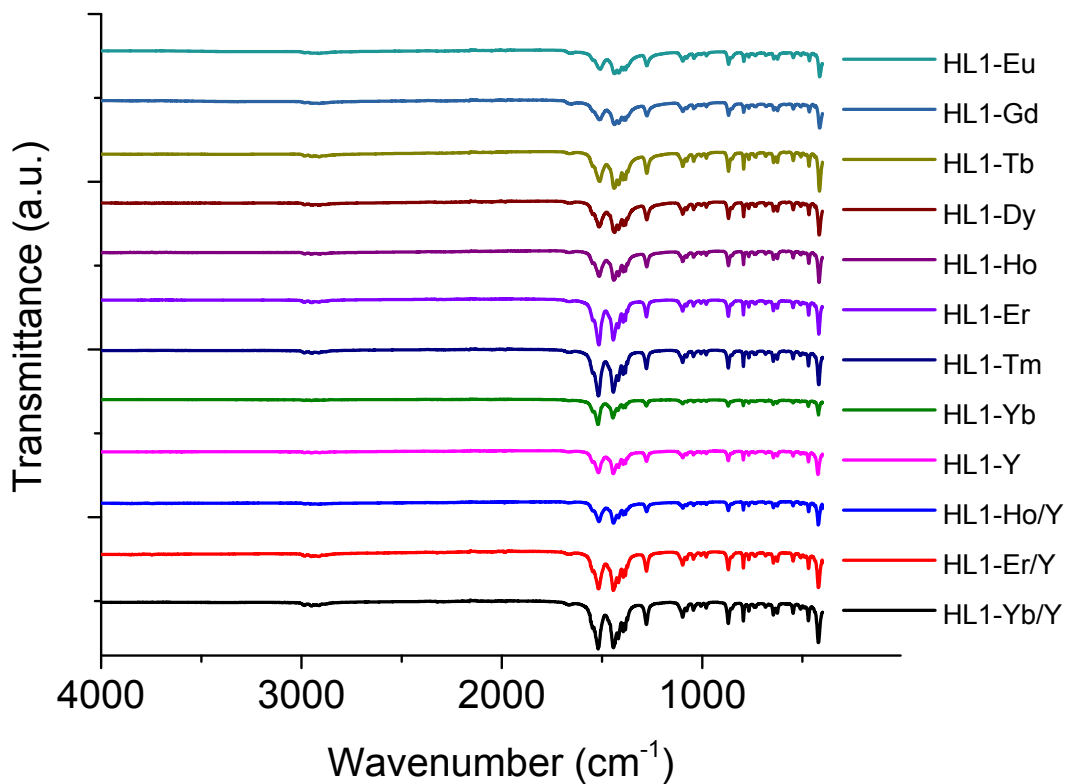
Found: 50.67 ppm

#### 4.4 Thermogravimetric analysis



**Figure S7.** TGA profile of **HL1-Eu**. The MOF is stable with no solvent loss up to ~400 °C.

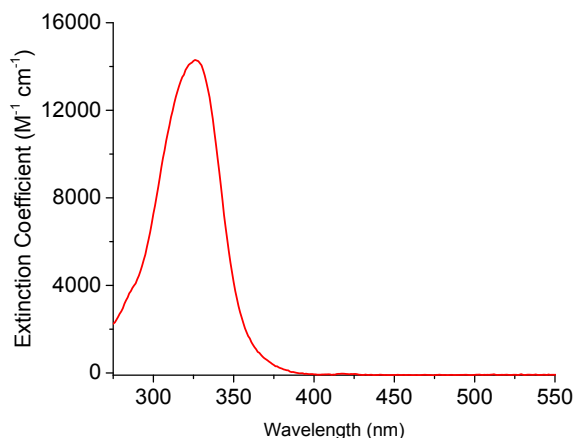
#### 4.5 Infrared spectroscopy



**Figure S8.** FTIR spectra of **HL1-Ln**, **HL1-Y**, and **HL1-Ln/Y** MOFs showing identical features.



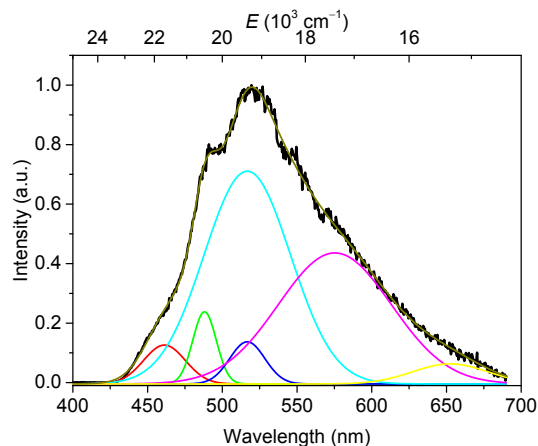
## 4.6 UV/vis absorption



**Figure S9.** UV/Vis absorption spectrum of H<sub>3</sub>tctb.

## 4.7 Photophysical studies

Luminescence data were collected on samples in the solid state placed in 2.4 mm i.d. quartz capillaries. Emission and excitation spectra were measured on a custom-designed Horiba Scientific Fluorolog 3 spectrofluorimeter equipped with either a visible photomultiplier tube (PMT) (220-850 nm, R928P; Hamamatsu) and a NIR PMT (950-1650 nm, H10330-75; Hamamatsu). Excitation and emission spectra were corrected for the instrumental functions. Luminescence lifetimes were determined under excitation at 355 nm provided by a Nd:YAG laser (YG 980; Quantel). The output signals from the detectors were fed into a 500 MHz bandpass digital oscilloscope (TDS 754C; Tektronix), transferred to a PC for data processing with the program Origin 8<sup>®</sup>. Luminescence lifetimes are averages of at least three independent measurements. Quantum yields were determined with the Fluorolog 3 spectrofluorimeter based on an absolute method with the use of an integration sphere (Model G8, GMP SA, Renens, Switzerland). Each sample was measured several times under comparable experimental conditions, varying the position of samples. Estimated experimental error for quantum yield determination is ~10 %.



**Figure S10.** Phosphorescence spectrum of **HL1-Gd** recorded in the solid state under ligand excitation at 360 nm (77 K, 50  $\mu$ s delay after the excitation flash). The spectrum was deconvoluted using Gaussian functions to obtain the zero-phonon component located at  $\sim$  461.3 nm.

#### 4.8. Y<sup>3+</sup> doping

ICP OES measurements:

##### **HL1-Yb/Y** [Yb<sub>0.5</sub>Y<sub>0.5</sub>(tctb)]:

1.75 mg sample was dissolved in 10.0 ml HNO<sub>3</sub> solution.

Calculated concentrations: Yb<sup>3+</sup> 22.58 ppm; Y<sup>3+</sup> 11.60 ppm.

Found: Yb<sup>3+</sup> 21.92 ppm, Y<sup>3+</sup> 10.94 ppm

##### **HL1-Er/Y** [Er<sub>0.5</sub>Y<sub>0.5</sub>(tctb)]:

1.89 mg sample was dissolved in 10.0 ml HNO<sub>3</sub> solution.

Calculated concentrations: Er<sup>3+</sup> 23.68 ppm; Y<sup>3+</sup> 12.58 ppm.

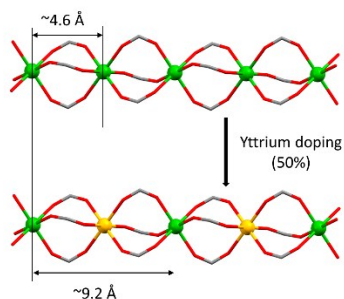
Found: Er<sup>3+</sup> 23.21 ppm, Y<sup>3+</sup> 11.47 ppm

##### **HL1-Ho/Y** [Ho<sub>0.5</sub>Y<sub>0.5</sub>(tctb)]:

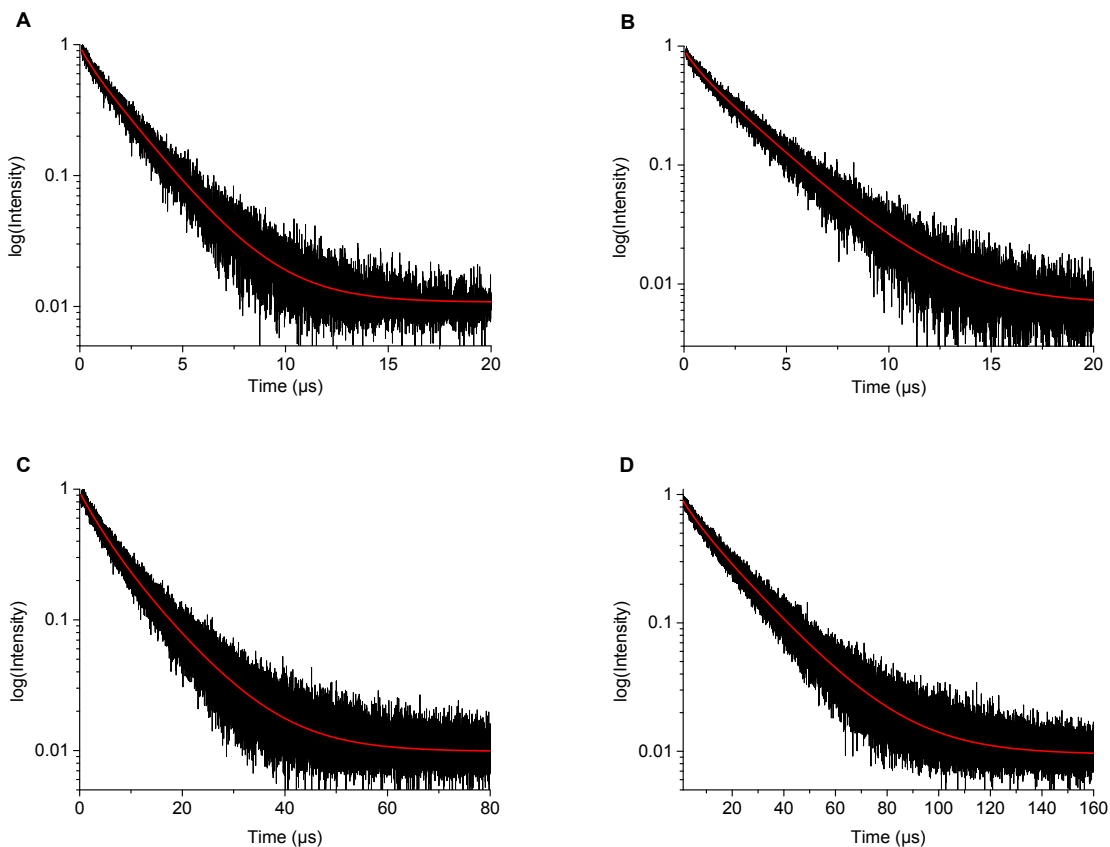
1.86 mg sample was dissolved in 10.0 ml HNO<sub>3</sub> solution.

Calculated concentrations: Ho<sup>3+</sup> 23.02 ppm; Y<sup>3+</sup> 12.41 ppm.

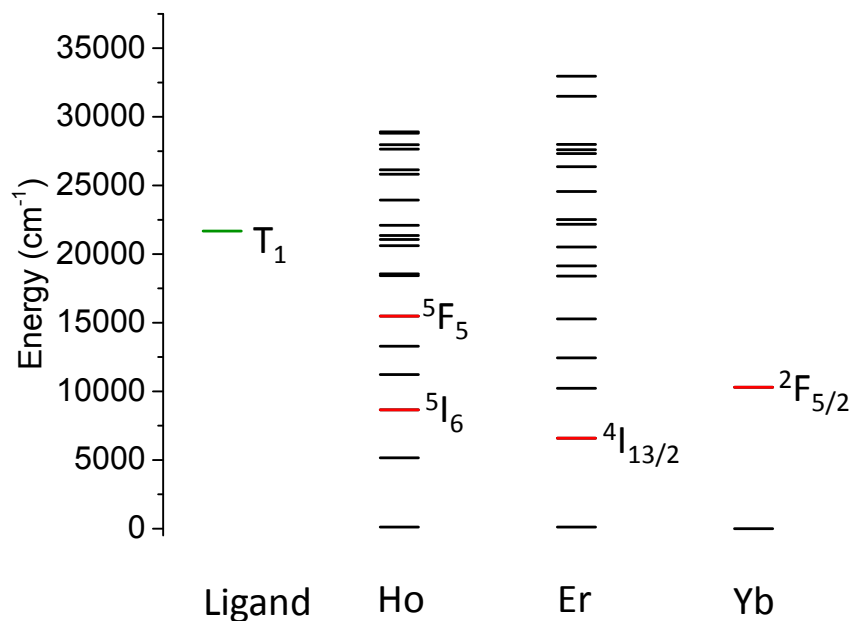
Found: Ho<sup>3+</sup> 21.37 ppm, Y<sup>3+</sup> 12.76 ppm.



**Figure S11.** Doping with 50% Yttrium theoretically double the inter-Ln distance in **HL1-Ln**.



**Figure S12.** Experimental luminescent decay curves (black traces) obtained upon excitation at 355 nm and monitoring emission at 980 nm or 1543 nm for  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$  MOFs, respectively. Red traces represent fitting curves using bi-exponential decay function. (A) **HL1-Er**, (B) **HL1-Er/Y**, (C) **HL1-Yb**, (D) **HL1-Yb/Y**. (Noted that three measurements were performed for each sample, but the curves are similar, so only one curve is shown for each sample).



**Figure S13.** Energy levels of the ligand (triplet state T<sub>1</sub>) and the lanthanide ions.<sup>10</sup> The red levels are emitting levels.

## References

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