Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supporting Information

NIR-to-NIR emission on a water-soluble $\{Er_6\}$ and $\{Er_3Yb_3\}$ nanosized molecular wheel

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Experimental Section

Synthesis of {[Ln_6(teaH)$_6$(NO_3)$_6$]: The synthetic procedure follows the previously reported.[S1] $Er(NO_3)_3 \cdot 6\ H_2O$ (0.6 mmol) was dissolved in MeOH/CH_2Cl_2 (5 mL : 15 mL), followed by the addition of triethanolamine (1.2 mmols) and triethylamine (4.8 mmols). After a few minutes the reaction mixture resulted in a clear pink solution. This solution was stirred for four hours. During this time, a small amount of precipitate formed. The solution was filtered and layered with Et_2O. After two days, pink crystals of [Er_6(teaH)$_6$(NO_3)$_6$] appeared in an approximate yield of 65 % (crystalline product). Unit cells from Ref. S1: a = b = 16.7413(3); c = 24.9834(8); α = β = 90; γ = 120; CCDC number: 1876163. Unit cells obtained: a = b = 16.7421(9); c = 24.9829(6); α = β = 90; γ = 120.

For {Yb_6} the same procedure was followed using 0.6 mmol of $Yb(NO_3)_3 \cdot 6\ H_2O$. Yield = 54 % (crystalline product).

For {Y_6} the same procedure was followed using 0.6 mmol of $Y(NO_3)_3 \cdot 6\ H_2O$. Yield = 58 % (crystalline product).

For {Er_3Yb_3} the same procedure was followed using 0.3 mmol of $Er(NO_3)_3 \cdot 6\ H_2O$ and 0.3 mmol of $Yb(NO_3)_3 \cdot 6\ H_2O$. ICP analysis: Calculated: Er (50 %) / Yb (50 %). Obtained: Er (44 %) / Yb (56 %). Yield = 72 % (crystalline product).

Sample preparation: For the luminescence studies, 5 mL of a 5.0 mg mL^{-1} solution of {Er_6} and {Er_3Yb_3} in water, was prepared. 5 mL of a 2.5 mg mL^{-1} solution of {Er_6} in deuterated water was also prepared.

For water stability studies, 10 mL of a 5 mg mL^{-1} solution in water, was prepared. The sample was kept in solution for one week before evaporated at room temperature using a controlled air flow. Result was an oil product which was dried on a Schlenk line under reduced pressure until the formation of the solid.

Characterisations:

Thermogravimetric analysis (TGA) was performed with a Q5000 TGA (TA instruments) equipment within a synthetic air atmosphere (heating rate of 10 °C min^{-1} and sample masses of approximately 8 mg). FTIR spectra were obtained in a Nicolet 6700 FT-IR Spectrometer (Thermo Scientific). PXRD diffractograms were obtained in a Rigaku Ultima IV Diffractometer using Cu Kα filtered radiation (λ = 1.5401 Å). ICP analysis was

performed in a 5110 ICP-OES Instrument (Agilent). NMR spectra were obtained at a Bruker AVANCE II 400 MHz spectrometer using D_2O as solvent. DRS spectra were obtained in a Cary 5000 UV-Vis-NIR spectrophotometer (Agilent). Luminescence properties were investigated in a 1 cm^{-1} optical glass cuvette in both water and deuterated solutions. Excitation was performed with a 980 nm laser diode. NIR emission was collected in a 90° configuration, using an IMA™ upconversion spectrometer (Photon Etc., Montreal, Canada) with a Princeton Instruments SP-2360 monochromator/spectrograph, a set of galvanometer mirrors, NIR emission filters and a BaySpec Nunavut deep-cooled InGaAs detector.

Crystallographic data collection and processing were performed at the X-Ray Core Facility at the University of Ottawa. Crystals were mounted on MiTeGen sample holders using Parabar oil. Data were collected on a Bruker Kappa ($\{Yb_6\}$) or Smart ($\{Er_3Yb_3\}$) ApexII diffractometer equipped with an ApexII CCD detector and a sealed-tube Mo Kα source (λ = 0.71073 A). During collection, the crystals were cooled to 200(2) K using a refrigerated, dry compressed air stream. Raw data collection and processing were performed with the Apex3 software package from Bruker.[S2] Initial unit cell parameters were determined from 36 data frames from select ω scans. Semi-empirical absorption corrections based on equivalent reflections were applied.[S3] Systematic absences in the diffraction data-set and unit-cell parameters were consistent with the assigned space group. $\{Er_3Yb_3\}$ crystallized as a merohedral twin, which was detected using XPrep, a component of the Apex3 software suite. Twinning was accounted for during the refinements outlined below. The initial structural solutions were determined using ShelxT direct methods,[S4] and refined with full-matrix least-squares procedures based on F^2 using ShelXle.[S5] Hydrogen atoms were placed geometrically and refined using a riding model. Twin fractions were also refined in ShelXle.

Figures and Tables

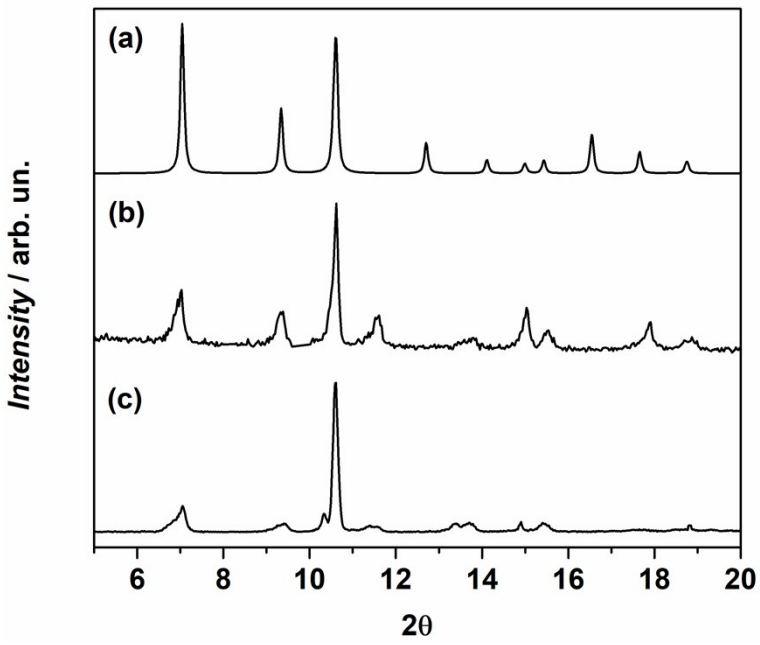

Figure S1: (a) Simulated PXRD pattern (CCDC number: 1876163) for $\{Er_6\}$ and experimental PXRD pattern for $\{Er_6\}$, (b) as synthesized and (c) after the solubilisation/drying procedure.

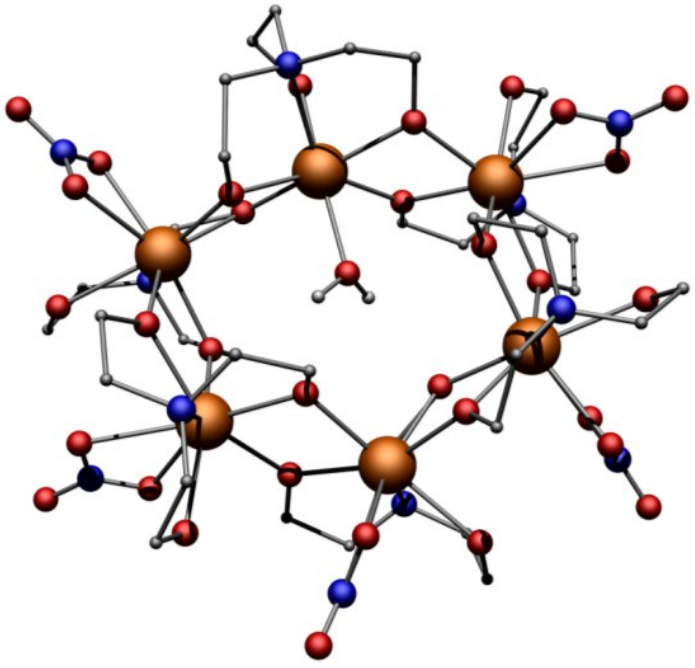

Figure S2: Molecular structure of $\{Yb_6\}$ cluster. Hydrogen (except those from the coordinated water molecule) and solvent atoms are omitted for clarity. Colour code: orange for ytterbium; red for oxygen; blue for nitrogen; dark grey for carbon and light grey for hydrogen.

Table S1: Crystallographic data and selected data collection parameters for $\{Yb_6\}$ and $\{Yb_3Er_3\}$.

Compound	**$\{Yb_6\}$**	**$\{Er_3Yb_3\}$**
Empirical formula	$C_{40}H_{86}N_{12}O_{39}Yb_6Cl_4$	$C_{43}H_{121}N_{12}O_{43}Eb_3Yb_3$
Formula weight	2539.24	2515.41
Crystal size, mm	0.24 x 0.26 x 0.30	0.395 × 0.236 × 0.16
CCDC number	1958096	1958091
Crystal system	Triclinic	Trigonal
Space group	*P* -1	*R* -3
Z	1	3
a, Å	12.1098(3)	16.7567(5)
b, Å	12.8247(3)	16.7567(5)
c, Å	24.7696(6)	25.0576(8)
α, °	97.196(2)	90
β, °	102.5490(10)	90
γ, °	98.363(2)	120
Volume, Å^3	3665.67(16)	6093.2(4)
Calculated density, Mg/m^3	2.301	2.057
Absorption coefficient, mm^{-1}	7.820	6.578
T (K)	200(2)	200(2)
F(000)	2420.0	3663.0
Θ range for data collection, °	3.254 to 55.12	3.244 to 72.912
Limiting indices	h = ±15 / k = ±16 / l = ±32	h = ±28 / k = ±28 / l = ±41
Reflections collected / unique	76587 / 16899	144511 / 6617
R(int)	0.0380	0.0576
Data / restraints / parameters	16899 / 433 / 924	6617 / 392 / 254
Goodness-of-fit on F^2	1.085	1.065
Final R indices [I>2σ(I)][a]	R1 = 0.0363, wR2 = 0.0714	R1 = 0.0242, wR2 = 0.0626
R indices (all data)	R1 = 0.0464, wR2 = 0.0749	R1 = 0.0275, wR2 = 0.0642
Largest diff. peak/hole, e·Å^{-3}	2.28/-1.96	1.86/-1.02

[a]Function minimized: $\sum w\left(F_o^2 - F_c^2\right)^2$. $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR_2 = [\sum \left(F_o^2 - F_c^2\right)^2 / \sum F_o^4]^{\frac{1}{2}}$

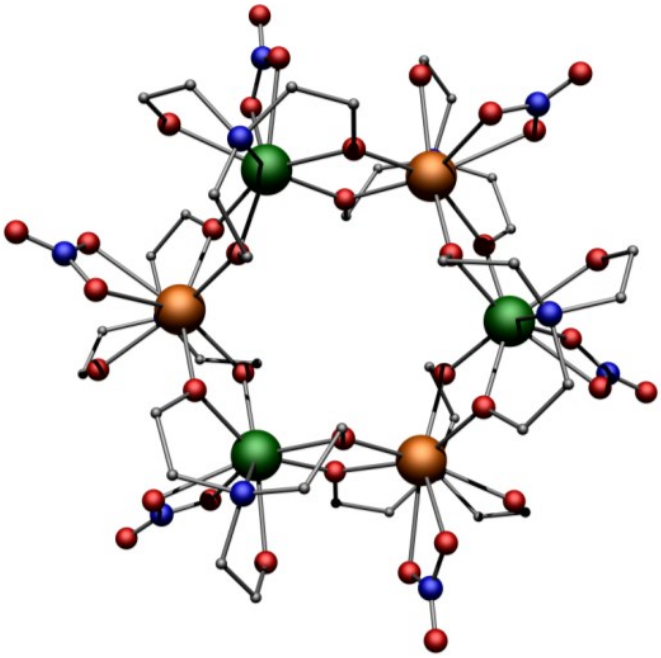

Figure S3: Molecular structure of $\{Er_3Yb_3\}$ cluster-aggregate. Hydrogen and solvent atoms are omitted for clarity. Colour code: green for erbium; orange for ytterbium; red for oxygen; blue for nitrogen and gray for carbon.

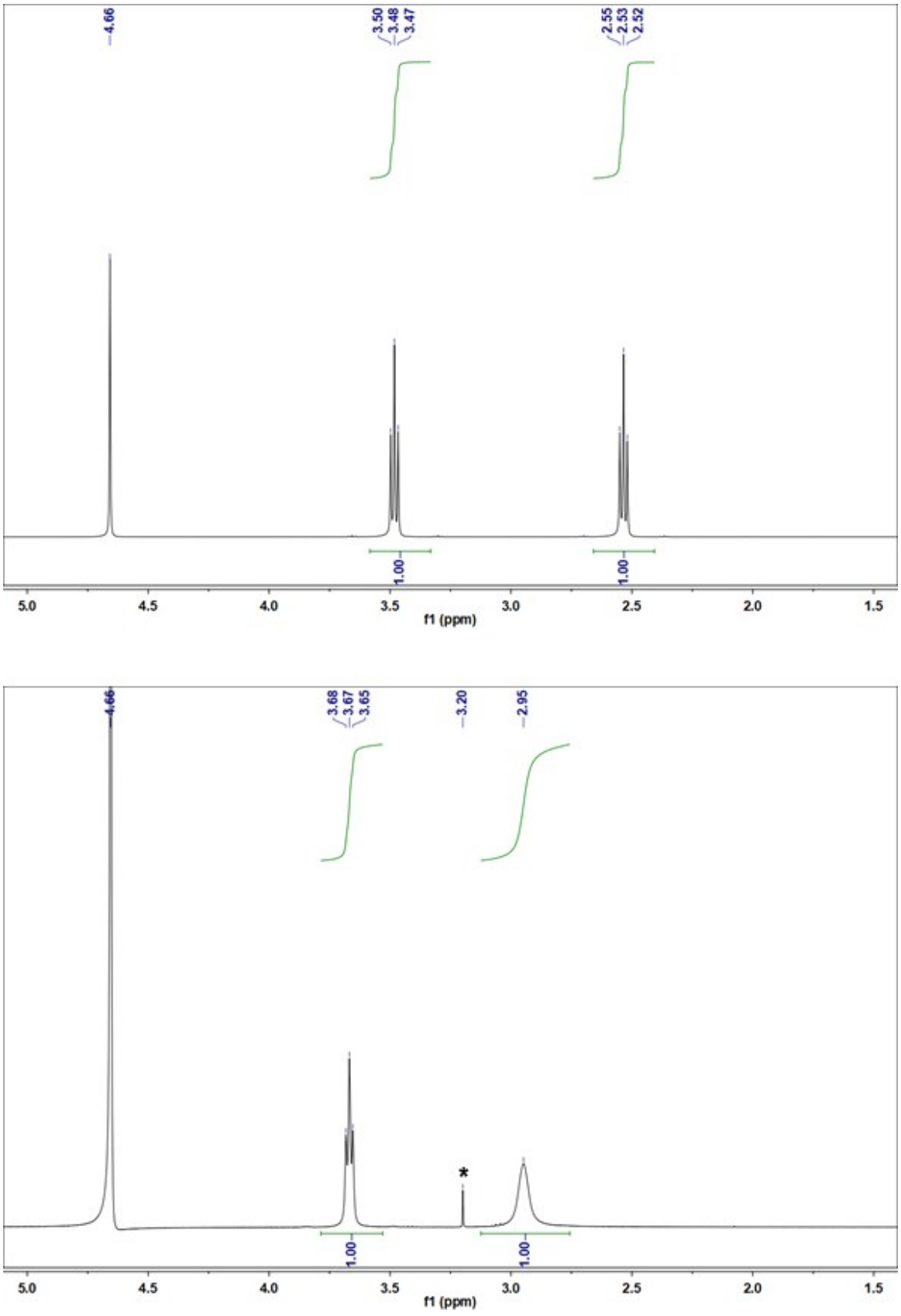

Figure S4: NMR spectra of (top) triethanolamine and (bottom) $\{Y_6\}$. *refers to the lattice MeOH solvent. Peak at 4.66 ppm refers to the residual water solvent.

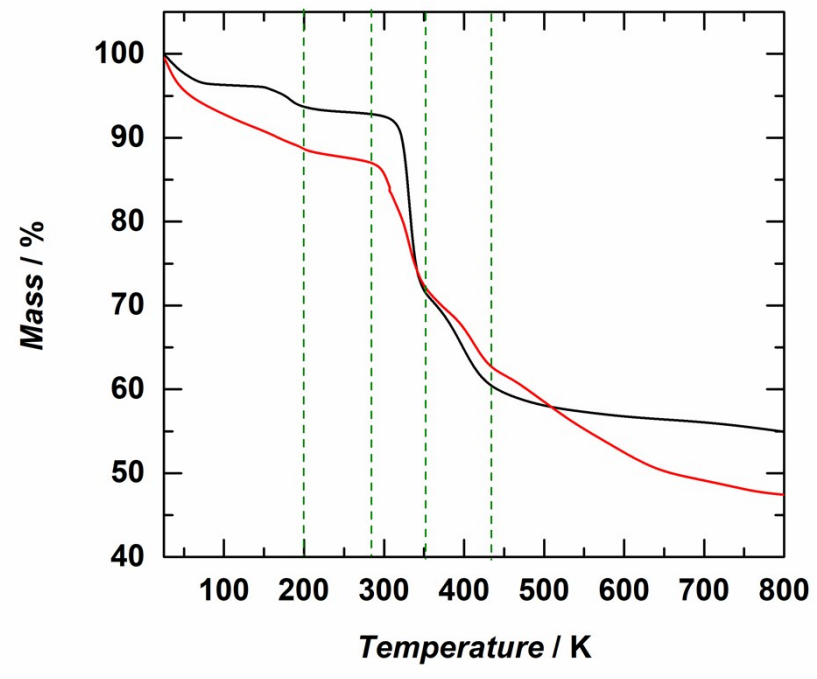

Figure S5: TGA curves for $\{Er_6\}$ as synthesized (black line) and after the solubilisation/drying procedure (red line). Green dashed lines are guidelines indicating the thermal decomposition processes.

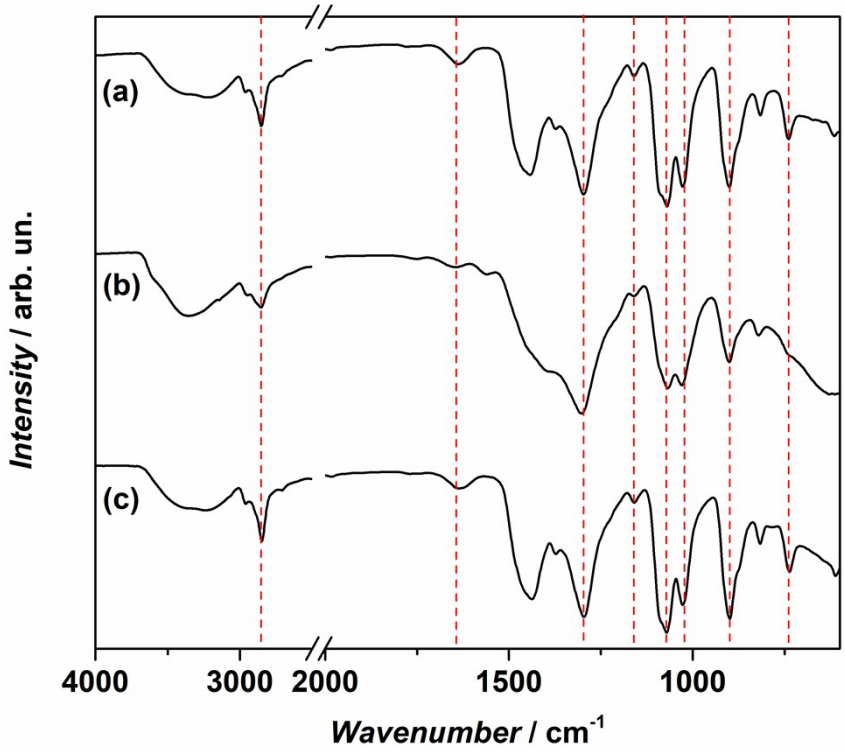

Figure S6: FTIR spectra of (a) $\{Er_6\}$ as synthesized, (b) after the solubilisation/drying procedure and (c) for $\{Er_3Yb_3\}$ as synthesized.

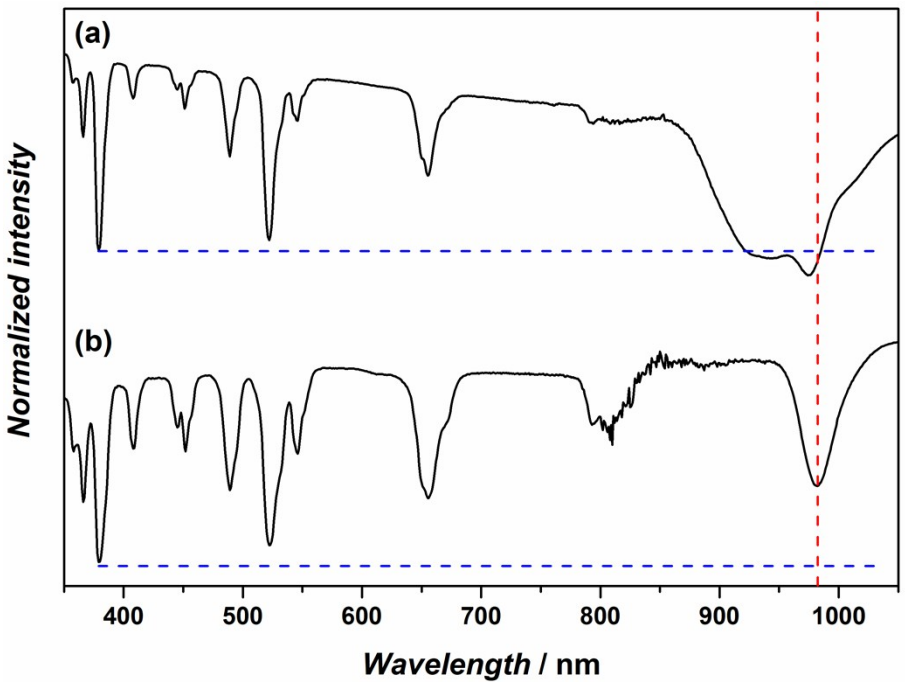

Figure S7: DRS spectra of (a) $\{Er_3Yb_3\}$ and (b) $\{Er_6\}$. The dashed red line is present as a guide to the eyes at 980 nm. The blue dashed lines are guides to the eyes evidencing the higher absorption cross-section for $\{Er_3Yb_3\}$ at the 980 nm region. Assignment of the bands on Table S2.

Table S2: Energy levels of $\{Er_6\}$ and $\{Er_3Yb_3\}$ as obtained *via* DRS (Figure S6).

Wavelength / nm	Wavenumber / cm^{-1}	Assignment
357	28011	$(^2K_{15/2}, {}^4G_{7/2}) \leftarrow {}^4I_{15/2}$
366	27322	$^4G_{9/2} \leftarrow {}^4I_{15/2}$
379	26385	$^4G_{11/2} \leftarrow {}^4I_{15/2}$
408	24509	$^2H_{9/2} \leftarrow {}^4I_{15/2}$
444	22522	$^4F_{3/2} \leftarrow {}^4I_{15/2}$
451	22172	$^4F_{5/2} \leftarrow {}^4I_{15/2}$
489	20449	$^4F_{7/2} \leftarrow {}^4I_{15/2}$
522	19157	$^2H_{11/2} \leftarrow {}^4I_{15/2}$
546	18315	$^4S_{3/2} \leftarrow {}^4I_{15/2}$
656	15243	$^4F_{9/2} \leftarrow {}^4I_{15/2}$
793	12610	$^4I_{9/2} \leftarrow {}^4I_{15/2}$
980	10204	$^4I_{11/2} \leftarrow {}^4I_{15/2}$ (Er^{3+}) $^7F_{5/2} \leftarrow {}^7F_{7/2}$ (Yb^{3+})

References

[S1] S. K. Langley, K. R. Vignesh, B. Moubaraki, G. Rajaraman, K. S. Murray, *Chem. Eur. J.* 2019, **25**, 4156-4165.

[S2] APEX Softward Suite v 2010 Bruker AXS Inc. Madison Wisconsin USA, 2010.

[S3] R. H. Blessing, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 1995, **51**, 33-38.

[S4] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, **A64**, 112-122.

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