SUPPLEMENTARY INFORMATION

Effect of the capping ligand on luminescent erbium(III) *β*-diketonate single-ion magnets

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Differential Scanning Calorimetry

The DSC curves of the studied complexes are shown in Fig. S1. For [Er(h)$_3$(bipy)], the endothermic effect attributable to pre-melting appears at 134ºC, followed by two second smaller endothermic effects at 153ºC and 165ºC –the latter presumably due to a definitive melting- and subsequent exothermic effects at 180ºC, which would correspond to decomposition. The curve for [Er(h)$_3$(bath)] shows an analogous thermal behaviour, with a single endotherm at 165ºC (melting) and decomposition in two steps, with maxima at 200ºC and 248ºC. Finally, [Er(h)$_3$(5NO$_2$phen)] shows a small endothermic effect at 165ºC (melting) and then slowly decomposes with a maximum at 219ºC. It should be noted that in these complexes, the melting temperature is mainly determined by the *β*-diketone (at 165ºC). When decomposition takes place in two steps (two exotherms, as in [Er(h)$_3$(bath)] curve), the first corresponds to the loss of the *β*-diketone ligands and the second to the loss of the diimide ligand.[1]

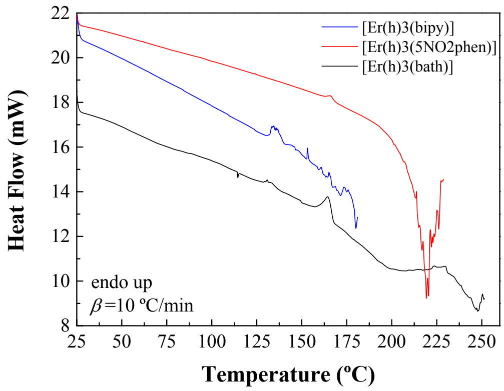

Fig S1. DSC curves for the three novel complexes.

Infrared spectroscopy

IR spectra of the complexes show the expected absorption bands for the *β*-diketonate ligand and the N,N-donor molecules (Fig. S2). The absorption bands have been identified in accordance with the literature.[2] The bands assigned to ring stretching modes CN, CC$_{str}$ (B$_1$ symmetry) and C=O, and ring 'breathing' modes are observed in the range 1597-1523 cm^{-1} and 1020–1015 cm^{-1}, respectively. They are shifted in comparison with those of the free ligands, suggesting are coordinated to erbium(III).[3]

IR spectra of the complexes under 900 cm^{-1} exhibit the absorption bands characteristic for coordinated N,N-donor molecules: 644, 740 and 762 cm^{-1} for the complex containing 2,2'-bipyridyne; 668, 737, 752 and 835 cm^{-1} for complex with 5-nitro-1,10-phenanthroline; and 575, 629, 703, 742, 763 and 807 cm^{-1} for the complex containing bathophenanthroline ligand.

Some bands under 580 cm^{-1} also offer evidence of the fact that coordination bonds have been formed between erbium and *β*-diketonate, and erbium and N,N-donor, respectively such as the one between 575 and 536 cm^{-1}, assigned to a ν(Er-N) vibration and that it appear at 411 cm^{-1}, which corresponds to ν(Er-O) vibration.

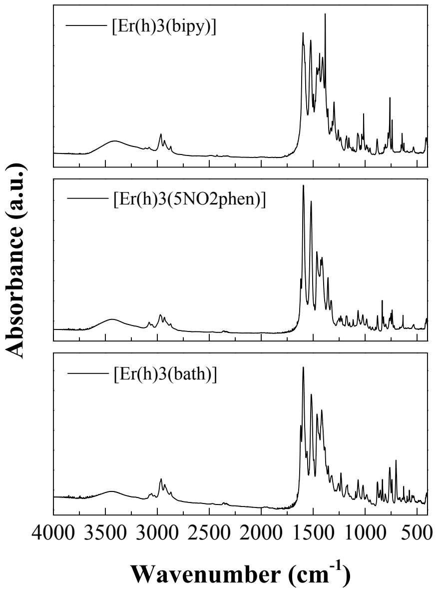

Fig S2 FTIR spectra of the novel complexes.

Raman spectroscopy

Fig. S3 shows the Raman spectra for the three complexes. Raman-active bands at approximately 410 cm^{-1} are tentatively assigned to ν(Er-N) modes. Whereas the complex with 5-nitro-1,10-phenanthroline ligand shows peaks at 1054 and 996 cm^{-1}, those of 2,2'-bipyridine and bathophenanthroline adducts show peaks at higher wavenumbers. Conversely, for the peaks at around 1300 cm^{-1} the behavior is reversed: they appear at higher wavenumbers for 5NO$_2$phen than for bipy and bath complexes. The peaks at around 1444 cm^{-1} are assigned to C=N ring vibrations. In the region around 1600 cm^{-1}, all the three complexes show C=O stretching frequencies shifted from those of the β-diketonate free ligands, thus providing good evidence that the lanthanide ion is coordinated through the oxygen atoms. The vibrational mode at around 700 cm^{-1}, assigned to CH out-of-plane for N,N-donors in the complexes, is also shifted from those which appear in their respective free ligands' spectra, giving evidence of the fact that nitrogen atoms are coordinated to Er^{3+}.

In the region above 2900 cm^{-1}, the C–H modes involving the aliphatic hydrogen atoms occurred at 2917-2931 and 2964 cm^{-1}.

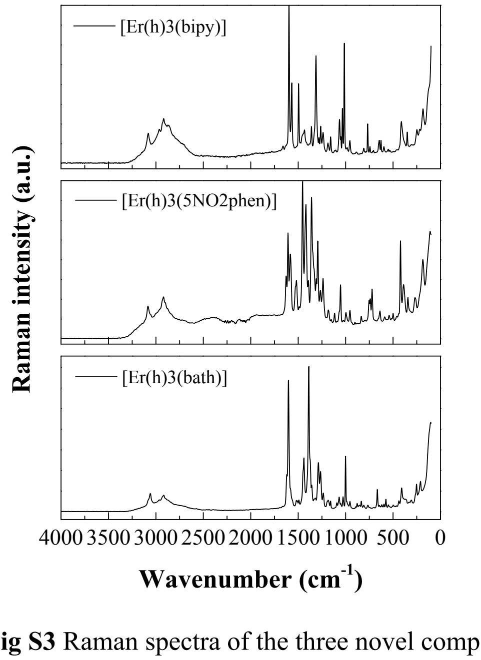

Fig S3 Raman spectra of the three novel complexes.

Comparison of PL emission intensities upon ligand excitation vs. Er^{3+} direct excitation

So as to compare the efficiency of the ligand-mediated excitation *vs*. that of Er^{3+} direct excitation in very reproducible conditions, additional steady state luminescence data were collected with a Jobin Yvon Fluorolog 3 spectrofluorometer equipped with a liquid nitrogen cooled InGaAs detector. In this case, the PL spectrum was recorded upon excitation at 350 nm and at $^2H_{11/2}$ (532 nm) Er^{3+} absorption with a 450W Xenon lamp and a 500 mW cw laser, respectively. The spectrum was acquired in the 850–1600 nm range with 1 s integration time at 1 nm step. The infrared emission spectra were corrected for the different source intensities at 350 and 522 nm (Fig. S4). It is noteworthy that upon excitation at 532 nm the photoluminescence intensity is half or a third than that gained upon excitation at 350 nm.

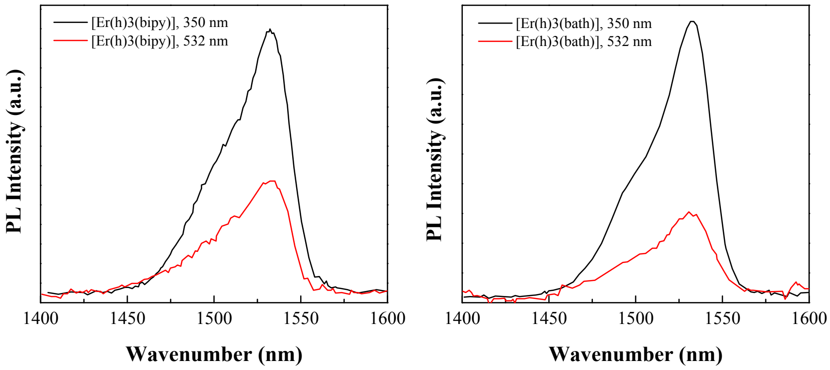

Fig S4 Comparison of NIR emission intensities for [Er(h)$_3$(bipy)] (*left*) and [Er(h)$_3$(bath)] (*right*) with a Jobin Yvon Fluorolog 3 spectrofluorometer equipped with a liquid nitrogen cooled InGaAs detector.

Lifetime measurements

The PL decays of the organic ligands has been measured after excitation with a high-repetition rate pulsed picosecond laser at 405 nm (Fig. S5), the same wavelength chosen for the visible PL spectra. The $S_1 \rightarrow S_0$ fluorescence decay from the ligand moieties was detected at about the maximum of the emission bands. A characteristic non-exponential decay was observed in all cases due to ligand-to-ligand or ligand-to-metal interactions. In addition to this, distribution of environments, which is typical in powder samples, can also contribute to the non-exponential character of the luminescence decay.

The PL decay times are consistent with a multiexponential equation, which can be useful to estimate an average lifetime that represents the decay rate of the complex.[4] The best fittings, made using instrument response function (IRF) reconvolution analysis and exponential component analysis with FAST® software by Edimburg Instruments, give an averaged decay of 1.35, 1.08 ns and 1.02 for [Er(h)$_3$(bipy)], [Er(h)$_3$(5NO$_2$phen)] and [Er(h)$_3$(bath)], respectively. The fact that [Er(h)$_3$(bipy)] shows a longer lifetime than the other two complexes accounts for its stronger PL emission in the visible region.

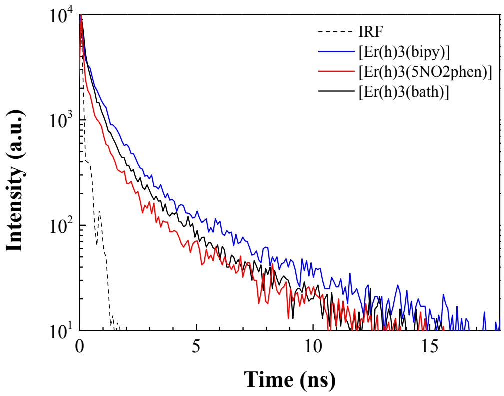

Fig S5 PL lifetime values for the ligand-associated emission in the visible region.

The NIR PL decay of the $^4I_{13/2}$ multiplet was measured after pumping at 980 nm with an OPO laser at 10 Hz repetition rate (Fig. S6). The decays show a single exponential behaviour, which can be observed as a linear dependence in the semi-log representations of Fig. S5. The obtained $^4I_{13/2}$ lifetimes for the three complexes, namely τ = 0.97, 1.08 and 1.16 µs for

[Er(h)$_3$(bipy)], [Er(h)$_3$(5NO$_2$phen)] and [Er(h)$_3$(bath)], respectively, are quite similar between them. These values, typical of lanthanide complexes,[5] are likely limited by "second-sphere" matrix interactions.

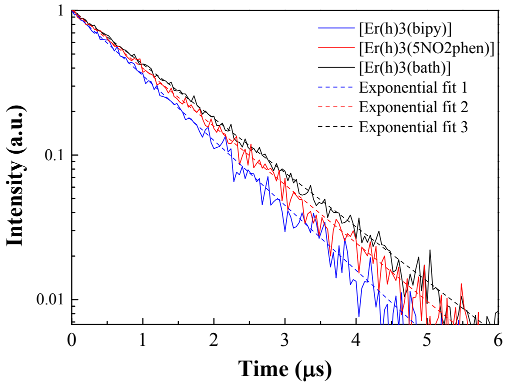

Fig S6 Er^{3+}:$^4I_{13/2}\rightarrow{}^4I_{15/2}$ emission lifetime measurements for the three complexes.

DC susceptibility measurements

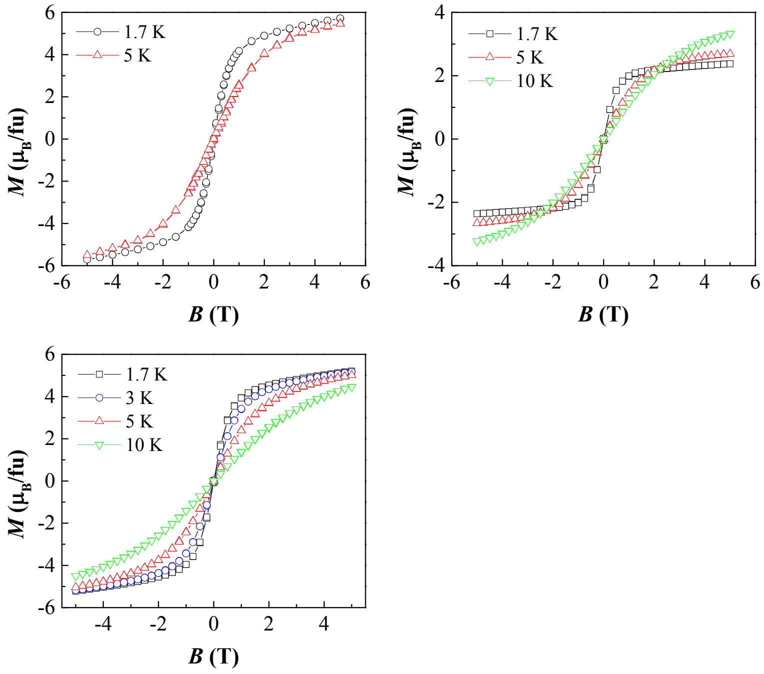

Fig S7 Hysteresis loops at different temperatures for [Er(h)$_3$(bipy)] (*top left*), [Er(h)$_3$(5NO$_2$phen)] (*top right*) and [Er(h)$_3$(bath)] (*bottom left*).

AC susceptibility measurements

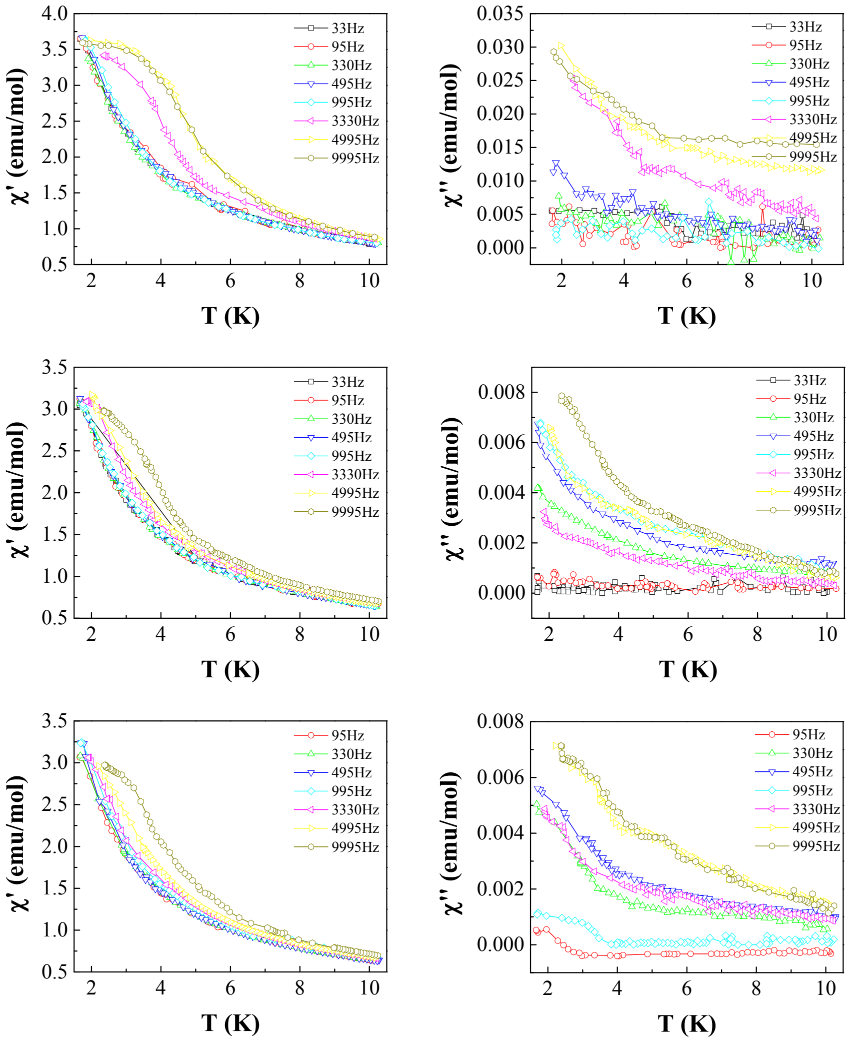

Fig. S8 In-phase (*left*) and out-of-phase (*right*) components of AC susceptibility at different frequencies in the 1.7 to 10K temperature range for [Er(h)$_3$(bipy)] (*top*), [Er(h)$_3$(5NO$_2$phen)] (*centre*) and [Er(h)$_3$(bath)] (*bottom*). H_{AC}=5 Oe; H_{DC}=0 Oe.

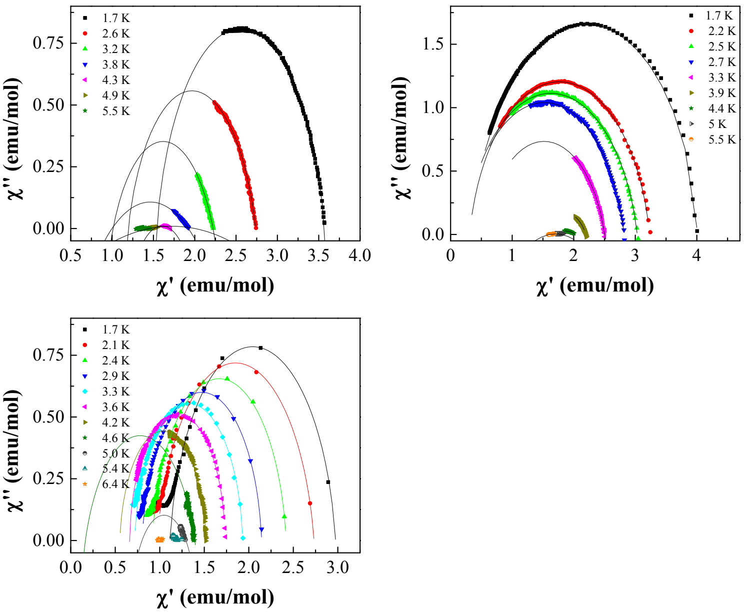

Fig S9 Argand diagrams and Debye fittings for [Er(h)$_3$(bipy)] (*top left*), [Er(h)$_3$(5NO$_2$phen)] (*top right*) and [Er(h)$_3$(bath)] (*bottom left*). H$_{AC}$=5 Oe; H$_{DC}$=1000 Oe.

References

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