Supplementary Information

Slow magnetic relaxation mechanisms in Erbium SIMs

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Infrared spectroscopy

The absorption bands with different intensities in the frequency range 1620–1459 cm⁻¹ correspond to aromatic ring vibrations of 2,2'-bipyridine and the (tfa) anions and to C=O groups of anions:¹ 1459 cm⁻¹, 1521 cm⁻¹ (aromatic ring), 1620 cm⁻¹ (C=O).

Analysis of the region below 1100 cm⁻¹ allows us to see the absorption bands characteristic of 2,2'bipyridine at 756, 738 and 645 cm⁻¹. Among these bands, the one which appears at 738 cm⁻¹ (an aromatic CH out-of-plane bending vibration) is appreciably red shifted (*vs.* that of free ligand) due to the perturbation induced by the coordination of this ligand to the metal ion.² The band that appears at around 585 cm⁻¹, which should assigned to a v(Er-N) vibration, also offers evidence of the fact that the coordination bonds have been formed between Er^{3+} and 2,2'-bipyridine.³

An important feature –provided that it is a fluorinated complex- is the occurrence of strong carbon–fluorine bands in the 1300 to 1100 cm^{-1} range, mainly those which appear at 1228 and 1141 cm⁻¹, assigned to CF₃ as (C–F) stretching modes.⁴

Finally, the absence of absorption in the 3500-3000 cm⁻¹ region, attributed to OH stretching vibrations, is the expected for a low amount of OH groups, as planned in the preparative conditions. The absence of bands at 2941 and 3054 cm⁻¹, assigned to aliphatic C-H and aromatic C-H, respectively, is also a noteworthy result.



Raman spectroscopy

The Raman spectrum of the complex (Figure S2) shows a strong multiple peak at 1600-1573 cm⁻¹, attributed to the C=N and C=O bonds from coordinated 2,2'-bipyridine and the (tfa) β -diketonate. Peaks at 1450 cm⁻¹ [v(C=C, C=N)], at 1325 cm⁻¹ [v(C=C) + δ (CH)], at 1025 cm⁻¹ (ring breathing) and at 780 cm⁻¹ [δ (CH)] are also characteristic of coordinated 2,2'-bipyridine.

As it happens in the infrared spectrum, the Raman spectrum do not shows the active high vibrational modes at >2500 cm⁻¹ that would be seen if C-H and O-H bonds were present in a significant amount.



¹H and ¹³C-NMR spectra

The ¹H-NMR spectrum for [Er(tfa)₃(bipy)] (Figure S3, *left*) displays one signal at 6.6-6.5 ppm, tentatively assigned to the methine group of the β -diketonate (tfa), and signals at 12.6 ppm and 11.3 ppm, 8.8-8.5 ppm and 8.0-7.7 ppm due to coordinated N,N-donor (bipy). Signals at 8.5 and 7.9 ppm are assigned to furyl-H protons. The weak absorption in the δ =2.5-2.1 ppm region is indicative of the protons adjacent to a carbonyl group in the β -diketonate. The chemical shift at around 1.2 ppm is typical of RCH₃.

The ¹³C-NMR spectrum of [Er(tfa)₃(bipy)] (Figure S3, *right*) shows a signal at around 44.9 ppm (septet), in good agreement with the value predicted using PerkinElmer ChemNMR[®] software for the α -carbon attached to the furyl functional group.



Figure S3. ¹H-NMR (*left*) and ¹³C-NMR (*right*) spectra for [Er(tfa)₃(bipy)].

TG/DTG/DTA analysis



Absorption spectra

The RT spectra derived from UV-Vis absorption of $[\text{Er}(\text{tfa})_3(\text{bipy})]$ in methanol diluted solutions and diffuse reflectance measurements for complex in powder form in the UV–Vis–NIR range (200–2000 nm) are shown in Figure S5. The broad and intense absorption bands in the range from 230 to 400 nm can be assigned to the electronic transitions from the ground-state level (π) S_0 to excited level (π^*) S_1 of the organic ligands.⁵ The absorption onset gives us an optical gap of 3.06 eV (405 nm), which is in agreement with the optical absorption threshold for the free ligand Htfa,⁵ while the main absorption peak is shifted 0.37 eV, at 3.46 eV (358 nm), indicating that the atomic configuration of the excited state is different from that corresponding to the ground state of the molecule.

Moreover, sharp peaks associated to *f*-*f* transitions of Er^{3+} can also be discerned (see inset in Figure S5 (*left*) and Figure S5 (*right*)). The bands correspond to the transitions from the fundamental state ${}^{4}\text{I}_{15/2}$ of Er^{3+} to the ${}^{4}\text{F}_{5/2}$, ${}^{4}\text{F}_{3/2}$ (~451 nm), ${}^{4}\text{F}_{7/2}$ (~488 nm), ${}^{2}\text{H}_{11/2}$ and ${}^{4}\text{S}_{3/2}$ (525-544 nm structure), ${}^{4}\text{F}_{9/2}$ (~655 nm), ${}^{4}\text{I}_{9/2}$ (~802 nm), ${}^{4}\text{I}_{11/2}$ (~977 nm) and ${}^{4}\text{I}_{13/2}$ (~1532 nm) excited states.⁶ The most intense transition corresponds to ${}^{4}\text{I}_{15/2}$ $\rightarrow^{2}\text{H}_{11/2}$ at 525 nm, which is a hypersensitive transition⁶ and its intensity is inversely related to the symmetry in the coordination sphere of the lanthanide (that is, the higher intensity the lower the symmetry in the coordination sphere).⁷ The bands which appear near 1675 nm and 1140 nm are associated to the second and third overtones of aromatic C-H stretching vibration, respectively.



Figure S5. Left: UV-Vis optical absorption spectrum for $[Er(tfa)_3(bipy]$ in $10^{-5}M$ and $10^{-3}M$ (*inset*) methanol diluted solutions; *right*: diffue reflectance spectrum of $[Er(tfa)_3(bipy)]$ in the UV–Vis–NIR range at RT. All transitions start from the ${}^4I_{15/2}$ ground state to the indicated levels.

Photoluminescence spectrum in the visible range

The emission of the novel Er^{3+} complex in the visible region (410-700 nm) has been studied under direct excitation of the organic ligands at λ_{exc} =405 nm (Figure S6). The organic part of the complex exhibits a broad emission with a maximum at 420 nm. Weak Er(III)-associated visible emission, arising from the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transition, can also be observed. Since the emission spectrum has been measured in powder, it is expected that it may be slightly red-shifted in comparison to that obtained in solution, as a result of the aggregation state.



Excitation spectrum

The excitation spectrum of the complex monitored at 1540 nm (see Figure S7) features a band at ca. 380 nm that can be ascribed to the tfa β -diketonate and another band at 340 nm associated to the 2,2'-bipyridine heterocyclic ligand.⁸ These bands can be attributed to their respective ligand-centered ($S_0 \rightarrow S_n$) transitions, and the shift between UV-Vis absorption and excitation peaks is consistent with the literature (e.g., [9]). Thus, aforementioned *antenna effect* sensitization mechanism is further confirmed.



Figure S7. Excitation spectrum (solid line) of [Er(tfa)₃(bipy)] complex and its deconvolution using modified Gaussian fits (dotted and dashed lines).

Lifetime measurements



Figure S8. Decay curve of the ligand emission upon excitation at λ =405 nm.

Magnetic measurements

STATIC MAGNETIC PROPERTIES



Figure S9. Hysteresis loops at different temperatures for [Er(tfa)₃(bipy)]. The solid lines are a guide to the eye.

DYNAMIC MAGNETIC PROPERTIES



Figure S10. In-phase (*left*) and out-of-phase (*right*) components of the ac susceptibility of $[Er(tfa)_3(bipy)]$ at different frequencies at $H_{ac} = 5$ Oe and $H_{DC} = 0$ Oe in the 1.7–10.6 K temperature range.



Figure S11. In-phase (*top*) and out-of-phase (*bottom*) components of the ac susceptibility at different frequencies in the 1.7–4.7 K temperature range for [Er(tfa)₃(bipy)] complex. Debye fittings are shown as dashed lines. H_{AC} =5 Oe; H_{DC} =1000 Oe.



Figure S12. In-phase (*top*) and out-of-phase (*bottom*) components of the ac susceptibility at different frequencies in the 1.7–4.7 K temperature range for [$\text{Er}(\text{tpm})_3(\text{bipy})$] complex. Debye fittings are shown as dashed lines. H_{AC}=5 Oe; H_{DC}=1000 Oe.

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