Supplementary Information:
Quantifying the magnetic nature of light emission

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Supplementary Figure S1: Energy level diagrams for trivalent europium and terbium. Free-ion energy diagrams for (a) Eu$^{3+}$ and (b) Tb$^{3+}$ showing the observed emission lines with their approximate center wavelengths. Note that the observed emission for each case originates from the lowest level in the $^5D_J$ manifold, i.e. $^5D_0$ for Eu$^{3+}$ and $^5D_4$ for Tb$^{3+}$. 
Supplementary Figure S2: Schematic of the three-layer system. Top layer 0 consists of air/vacuum (with refractive index $n_0 = 1$), layer 1 contains the emitters ($n_1$), and layer 2 is a quartz substrate ($n_2 = 1.5$). The central emitting layer has a thickness of $D$. The emitter is located a distance $d$ away from the 1, 2 interface such that the distance from the 1, 0 interface is $s = D - d$. Experimentally, we observe emission into the substrate half-space, but to derive the normalized local density of optical states, we use a reciprocal illumination scheme based on the depicted plane waves of s- and p-polarization.
Supplementary Figure S3: Dependence of normalized energy spectra on numerical aperture (NA). Curves show the normalized spectra obtained after integrating the experimental BFP spectra of Eu\(^{3+}:Y_2O_3\) over the momentum ranges accessible for different NA values. Note that the use of a high NA oil immersion objective enables the direct measurement of light emission above the critical angle (i.e. \(k_\parallel > k_0\)), which helps to improve the accuracy of our fitting analysis. This high NA also helps to illustrate an important difference between the angular emission patterns of electric dipole (ED) and magnetic dipole (MD) transitions. In thin luminescent films, the emission of isotropic MDs tends to be concentrated near the critical angle. For small collection angles, the normalized energy spectra appears to be independent of NA as shown by the NA=0.1 and NA=0.5 curves. However, as the collection NA approaches and exceeds 1, there is a significant increase in the emission observed from the \(^{5}D_0 \rightarrow ^{7}F_1\) MD transitions. Such dependence on the collection system complicates the interpretation of energy spectra. Our analysis of the full BFP energy-momentum spectrum, as described in the main text, is directed at overcoming this limitation and leveraging the angular dependence of ED and MD emission to quantify the underlying transitions.
Supplementary Figure S4: Quantifying the strongly mixed transitions in Tb³⁺:Y₂O₃ by energy-momentum spectroscopy. (a,b) Experimental energy- and momentum-resolved BFP spectra for s- and p- polarization, respectively. (c) Integrated energy spectrum of the total observed emission (N, black line) decomposed into the contributions from ED (N_{ED}, blue line) and MD (N_{MD}, red line) transitions. (d,e) Theoretical BFP spectra for s- and p-polarization, respectively, produced using fits to equation (1) in the main text. (f) Spectrally-resolved intrinsic emission rates, A_{ED} (solid blue line) and A_{MD} (solid red line), deduced from fitting analysis together with their 95% confidence intervals (dashed lines). (g) Momentum cross sections showing that experimental data (solid lines) from strongly mixed transitions can be readily resolved by theoretical fits (dashed lines). Emission at 543.8 nm is majority magnetic (MD = 58.4 ± 1.1%), whereas emission at 551.5 nm is majority electric (MD = 41.7 ± 0.8%). Emission at 548.5 nm is almost equal parts electric and magnetic (MD = 51.7 ± 0.9%). Note that a 10% difference in fractional magnetic dipole contribution results in a markedly different momentum-distributed luminescence.
**Supplementary Figure S5: Effect of index and thickness variations on fit values.** Spectrally-resolved intrinsic emission rates, $A_{ED}$ (dashed lines) and $A_{MD}$ (solid lines), for (a) Eu$^{3+}$:Y$_2$O$_3$ and (b) Tb$^{3+}$:Y$_2$O$_3$ obtained by fitting their energy-momentum spectra. Black curves present the fits obtained using the refractive index and thickness values measured from the central deposition region where luminescence data was acquired ($n_r = 1.77$, $D = 21.6$ nm for Eu$^{3+}$ and $n_r = 2.00$, $D = 14.8$ nm for Tb$^{3+}$). Blue and red curves show the fits obtained when using the maximal deviations from these values as measured at the outer edges of the deposition region ($n_r = 1.82$, $D = 19.0$ nm and $n_r = 1.72$, $D = 24.3$ nm for Eu$^{3+}$; $n_r = 1.97$, $D = 12.4$ nm and $n_r = 1.95$, $D = 16.5$ nm for Tb$^{3+}$).
Supplementary Methods

The Electric and Magnetic Local Density of Optical States

This section provides a detailed derivation of the analytical theory used to model the spontaneous emission from electric and magnetic dipole emitters. These expressions are used in the main text to decompose light emission into parts originating from electric and magnetic dipole transitions, determine the underlying transition dipole moments, and measure the electric and magnetic local density of optical states in an unknown environment.

Homogeneous optical environment

Within a homogeneous isotropic medium defined by an absolute permittivity \( \epsilon = \epsilon_r \epsilon_0 \) and absolute permeability \( \mu = \mu_r \mu_0 \), the total spontaneous emission rates (i.e. the Einstein \( A \) coefficients) for isotropic electric dipole (\( A_{ED} \)) and magnetic dipole (\( A_{MD} \)) transitions are given by Fermi’s golden rule as follows\(^{34,35} \):

\[
A_{ED}(\omega) = \rho_0(\omega) \frac{\pi \omega^3 |\mu_{ED}(\omega)|^2}{3\hbar \epsilon},
\]

\[
A_{MD}(\omega) = \rho_0(\omega) \frac{\pi \omega^3 |\mu_{MD}(\omega)|^2}{3\hbar \mu},
\]

where \( \omega \) is emission frequency, \( \rho_0(\omega) = \omega^2 (\epsilon \mu)^{3/2} / \pi^2 \) is the density of electromagnetic modes in the emitter medium, and \( \mu_{ED}(\omega) \) and \( \mu_{MD}(\omega) \) are the electric and magnetic transition dipole moments, respectively. Note that the electric dipole moment has units of \( C \cdot m \), whereas the magnetic dipole moment has units of \( A \cdot m^2 \).

Inhomogeneous optical environment

When placed in an inhomogeneous environment, spontaneous emission rates and patterns are modified by variations in the local density of optical states. The emission rate (\( \Gamma \)) into each mode defined by a frequency (\( \omega \)), a polarization (\( s \) or \( p \)), and a direction given by the in-plane momentum (\( k_\parallel \)) can be written as follows for electric and magnetic dipole transitions:

\[
\Gamma_{s,p}^{ED}(\omega, k_\parallel) = A_{ED}(\omega) \tilde{\rho}_{s,p}^{ED}(\omega, k_\parallel),
\]

\[
\Gamma_{s,p}^{MD}(\omega, k_\parallel) = A_{MD}(\omega) \tilde{\rho}_{s,p}^{MD}(\omega, k_\parallel)
\]

where \( \tilde{\rho}_{s,p}^{ED}(\omega, k_\parallel) \) and \( \tilde{\rho}_{s,p}^{MD}(\omega, k_\parallel) \) are the normalized electric and magnetic local density of optical states defined as:

\[
\tilde{\rho}_{s,p}^{ED}(\omega, k_\parallel) = \frac{\rho_{s,p}^{ED}(\omega, k_\parallel)}{\rho_0(\omega)}, \quad \tilde{\rho}_{s,p}^{MD}(\omega, k_\parallel) = \frac{\rho_{s,p}^{MD}(\omega, k_\parallel)}{\rho_0(\omega)}.
\]

Equations (S1) to (S5) define the electric and magnetic local density of optical states (\( \rho_{ED} \) and \( \rho_{MD} \)). Next, we derive analytical expressions for the normalized local densities of optical states.

Reciprocity formulation of \( \tilde{\rho}_{s,p}^{ED} \) and \( \tilde{\rho}_{s,p}^{ED} \)

Consider the general case where an emitter is embedded in a material with refractive index \( n_1 \) in an inhomogeneous environment. We wish to determine the far-field emission into a half-space defined by the positive \( z \) axis: \( k_{z2} = k_{z2} \hat{z} \), with \( k_{z2} \geq 0 \), and \( k_{z2} \) is the \( z \) component of the wave vector in the far-field medium with refractive index \( n_2 \). We define the far-field modes in terms of their momentum components in the \( xy \) plane: \( k_\parallel = k_x \hat{x} + k_y \hat{y} \).
Note that $k_{z2}$ and $k_{\parallel}$ are related through $k_2 = \sqrt{k_{z2}^2 + k_{\parallel}^2} = n_2 k_0$, where $k_2$ and $k_0$ are the wave numbers in the far-field medium and in vacuum respectively, and $k_{\parallel} = |k_{\parallel}|$.

To calculate the normalized local density of optical states $\tilde{\rho}^{s,p}_{ED}$ and $\tilde{\rho}^{s,p}_{MD}$, we exploit the reciprocity theorem. We determine the enhanced (or suppressed) emission rate into each mode from the enhanced (or suppressed) local field at the emitter’s position for illumination by that mode:

$$\tilde{\rho}^{s,p}_{ED}(\omega, k_{\parallel}) = \frac{1}{8\pi k_2^2 k_{z2} n_1} \left( \frac{E_x(\omega, k_{\parallel})}{E_0^{s,p}} \right)^2 + \left( \frac{E_y(\omega, k_{\parallel})}{E_0^{s,p}} \right)^2 + \left( \frac{E_z(\omega, k_{\parallel})}{E_0^{s,p}} \right)^2, \quad (S6)$$

$$\tilde{\rho}^{s,p}_{MD}(\omega, k_{\parallel}) = \frac{1}{8\pi k_2^2 k_{z2} n_1^3} \left( \frac{B_x(\omega, k_{\parallel})}{B_0^{s,p}} \right)^2 + \left( \frac{B_y(\omega, k_{\parallel})}{B_0^{s,p}} \right)^2 + \left( \frac{B_z(\omega, k_{\parallel})}{B_0^{s,p}} \right)^2. \quad (S7)$$

Here, $E_0^{s,p}$ and $B_0^{s,p}$ are the electric and magnetic field amplitudes for incident plane waves with parallel momentum $k_{\parallel}$ and either $s$- or $p$-polarization. $E_x$, $E_y$, $E_z$, $B_x$, $B_y$ and $B_z$ are the Cartesian components of the resulting local field at the emitter position. These equations are valid for any (locally) inhomogeneous environment composed of reciprocal (linear, time-invariant) media.

Although here we use the equations outlined above, which we feel are particularly intuitive, the problem of emission in a layered geometry has previously been approached and solved in a variety of other ways.

**Fresnel reflection and transmission coefficients**

The specific three-layer system studied here is shown in Supplementary Figure S3. To calculate the local electric and magnetic fields at the emitter, we use the following reflection ($r$) and transmission ($t$) coefficients for the incident plane waves:

$$t_{21}^s = \frac{2k_{z2}}{k_{z2} + k_{z1}}, \quad t_{21}^p = \frac{2n_1^2 k_{z2}}{n_1^2 k_{z2} + n_2^2 k_{z1} n_1}, \quad (S8)$$

$$r_{10}^s = \frac{k_{z1} - k_{z0}}{k_{z1} + k_{z0}}, \quad r_{10}^p = \frac{n_0^2 k_{z1} - n_1^2 k_{z0}}{n_0^2 k_{z1} + n_1^2 k_{z0}}, \quad (S9)$$

$$r_{12}^s = \frac{k_{z1} - k_{z2}}{k_{z1} + k_{z2}}, \quad r_{12}^p = \frac{n_0^2 k_{z1} - n_1^2 k_{z2}}{n_0^2 k_{z1} + n_1^2 k_{z2}}. \quad (S10)$$

In the literature, there are several different conventions for the definition of the Fresnel coefficients. Here, we define all coefficients for both $s$- and $p$-polarization in terms of the electric field. As per the sign convention used in Ref. 33, the $p$-polarized reflection is also defined such that the direction of the transverse magnetic field is conserved when the reflected phase is zero.

**Normalized electric local density of optical states**

Using equations (S8) to (S10), we can derive from equation (S6) the following analytical expressions for the normalized local electric density of optical states:

$$\tilde{\rho}^s_{ED}(\omega, k_{\parallel}) = \frac{1}{8\pi k_2^2 k_{z2} n_1} \left| \frac{k_2}{k_{\parallel}} \frac{t_{21}^s e^{ik_{z1}d}}{1 - r_{10}^s r_{12}^p e^{2ik_{z1}d}} \right|^2 \left( \frac{k_{z1}}{k_1} \left( 1 - r_{10}^p e^{2ik_{z1}d} \right)^2 + \frac{k_{\parallel}}{k_1} \left( 1 + r_{10}^p e^{2ik_{z1}d} \right)^2 \right), \quad (S11)$$

$$\tilde{\rho}^p_{ED}(\omega, k_{\parallel}) = \frac{1}{8\pi k_2^2 k_{z2} n_1} \left| \frac{k_2}{k_{\parallel}} \frac{t_{21}^p e^{ik_{z1}d}}{1 - r_{10}^s r_{12}^p e^{2ik_{z1}d}} \right|^2 \left( 1 + r_{10}^s e^{2ik_{z1}d} \right)^2. \quad (S12)$$
Normalized magnetic local density of optical states

Likewise, we can derive from equation (S7) the following analytical expressions for the normalized local magnetic density of optical states:

\[ \tilde{\rho}^{p}_{MD}(\omega, k_{\parallel}) = \frac{1}{8\pi k_{2}^{2}k_{2} n_{1}} \left| \frac{r_{21}^{p}e^{ik_{z}zD}}{1 - r_{10}^{p}r_{12}^{p}e^{2ik_{z}D}}(1 + r_{10}^{p}e^{2ik_{z}D}) \right|^2, \]  

(S13)

\[ \tilde{\rho}^{s}_{MD}(\omega, k_{\parallel}) = \frac{1}{8\pi k_{2}^{2}k_{2} n_{1}} \left| \frac{t_{21}^{s}e^{ik_{z}zD}}{1 - r_{10}^{s}r_{12}^{s}e^{2ik_{z}D}} \right|^2 \left( \frac{k_{z1}}{k_{1}}(1 - r_{10}^{s}e^{2ik_{z}D}) + \frac{k_{1}}{k_{1}}(1 + r_{10}^{s}e^{2ik_{z}D}) \right)^2. \]  

(S14)

Based on the conventions defined above, equations (S13) and (S14) for magnetic dipoles can also be obtained by simply interchanging \( s \)- and \( p \)-polarization in equations (S11) and (S12) for electric dipoles.

Quantifying the emission in a known optical environment

Having derived expressions for \( \tilde{\rho}^{s,p}_{ED}(\omega, k_{\parallel}) \) and \( \tilde{\rho}^{s,p}_{MD}(\omega, k_{\parallel}) \) in a three-layer system, we can thus fit the observed counts \( N(\omega, k_{\parallel}) \) from our known thin film samples to a superposition of the rates given by equations (S3) and (S4):

\[ N^{s,p}(\omega, k_{\parallel}) = C_{1} \left[ \tilde{\rho}^{s,p}_{ED}(\omega, k_{\parallel})A_{ED}(\omega) + \tilde{\rho}^{s,p}_{MD}(\omega, k_{\parallel})A_{MD}(\omega) \right]. \]  

(S15)

This fitting procedure determines the spectrally-resolved intrinsic emission rates \( A_{ED}(\omega) \) and \( A_{MD}(\omega) \), and thus the transition dipole moments \( \mu_{ED}(\omega) \) and \( \mu_{MD}(\omega) \), up to an experimental proportionality constant \( C_{1} \). For this analysis, we make two approximations: first, that each ion is an isotropic emitter; second, that the ensemble of ions is effectively homogeneous, i.e. the excitation of each emitter results in the same emission spectrum. Although there is inhomogeneous broadening and ions occupy two lattice sites in \( Y_{2}O_{3} \), these approximations have accurately predicted the modified emission spectra of \( Eu^{3+}:Y_{2}O_{3} \) in previous experiments\(^28 \), and are also supported by evidence of strong energy transfer between sites\(^31 \).

In the main text, we show that energy-momentum analysis can effectively quantify the spectrally distinct electric and magnetic dipole transitions in \( Eu^{3+}:Y_{2}O_{3} \). In Supplementary Figure S4, we further demonstrate that this analysis can distinguish electric and magnetic dipole contributions to the strongly mixed \( 5D_{4} \rightarrow 7F_{5} \) transitions in \( Tb^{3+}:Y_{2}O_{3} \). As shown in Supplementary Figure S1, \( 5D_{4} \) is the lowest level in the \( 5D_{J} \) manifold for \( Tb^{3+} \), whereas \( 5D_{0} \) is the lowest level for \( Eu^{3+} \). Thus, for both materials studied here, the observed emission originates from a single excited level.

The accuracy of this analysis is coupled to the accuracy with which we can independently characterize the local optical environment for each sample, especially the thickness and refractive index of the emitting layer. As described in the Methods Section of the main text, the thickness of the luminescent layers was measured \textit{in situ} using a quartz crystal microbalance and then confirmed \textit{ex situ} via ellipsometry on silicon reference samples. In the central deposition region from which all luminescent data was acquired, the \( Eu^{3+}:Y_{2}O_{3} \) film had a measured thickness \( (D) \) of 21.6 nm with refractive index \( (n_{r}) \) of 1.77 to within the accuracy determined from the ellipsometer’s repeatability specification. Similarly, in the central deposition region, the \( Tb^{3+}:Y_{2}O_{3} \) film had thickness of 14.8 nm with a refractive index of 2.00. However, due to the angled configuration of the co-sputtering targets with respect to the rotating substrate holder, there is a variation in the composition and thickness of deposited films across one dimension. For the \( Eu^{3+}:Y_{2}O_{3} \) sample, the maximal observed deviations over the entire deposition region were \( D = 19 \) nm, \( n_{r} = 1.82 \) and \( D = 24.3 \) nm, \( n_{r} = 1.72 \). Likewise, for the \( Tb^{3+}:Y_{2}O_{3} \) sample, the maximal observed deviations were \( D = 12.4 \) nm, \( n_{r} = 1.97 \) and \( D = 16.5 \) nm, \( n_{r} = 1.95 \). To examine the implications of such variations on the accuracy of our analysis, we refit the experimental data using these maximal deviation values. Supplementary Figure S5 compares the intrinsic rates, \( A_{ED} \) and \( A_{MD} \), inferred from these extreme cases to those obtained with the central region values. The effects of these variations are still relatively small. In terms of normalized units, the \( A_{ED} \) variations are within 0.02 for \( Eu^{3+} \) and 0.01 for \( Tb^{3+} \), while the \( A_{MD} \) variations are within 0.05 for \( Eu^{3+} \) and 0.08 for \( Tb^{3+} \). Note that the greater variations observed for \( A_{MD} \) stems from the greater sensitivity of MD transitions on the local refractive index. As shown in equations (S1-S2) and (S6-S7), \( A_{MD} \) scales with \( n_{r}^{3} \), whereas \( A_{ED} \) scales linearly with \( n_{r} \).
Measuring the local density of optical states in an unknown environment

After quantifying the electric and magnetic dipole transitions in a given material, we can then use these transitions to probe the electric and magnetic local density of states in a new optical environment. Using equation (S15), we can determine \( \tilde{\rho}_{s,p}^{\text{ED}}(\omega, k_{\parallel}) \) and \( \tilde{\rho}_{s,p}^{\text{MD}}(\omega, k_{\parallel}) \) with known values for \( A_{\text{ED}}(\omega) \) and \( A_{\text{MD}}(\omega) \), provided that the electric and magnetic density of states vary slowly with frequency compared to the intrinsic rates. Therefore, this procedure is particularly robust when we examine the emission from a pair of spectrally close electric and magnetic dipole transitions, such as the 580.8 nm and 582.2 nm Eu\(^{3+} \) transitions discussed in the main text. Consider two momentum cross-sections, \( N_{s,p}(\omega_0 + \Delta, k_{\parallel}) \) and \( N_{s,p}(\omega_0 - \Delta, k_{\parallel}) \), acquired near a central frequency \( (\omega_0) \). For these narrow transitions the intrinsic emission rates vary much faster with frequency than the density of optical states, and a linear approximation can be used to calculate \( \tilde{\rho}_{s,p}^{\text{ED}}(\omega_0, k_{\parallel}) \) and \( \tilde{\rho}_{s,p}^{\text{MD}}(\omega_0, k_{\parallel}) \) as follows:

\[
\tilde{\rho}_{s,p}^{\text{ED}}(\omega_0, k_{\parallel}) = \frac{C_1 N_{s,p}(\omega_0 + \Delta, k_{\parallel}) A_{\text{MD}}(\omega_0 - \Delta) - N_{s,p}(\omega_0 - \Delta, k_{\parallel}) A_{\text{MD}}(\omega_0 + \Delta)}{C_2 A_{\text{ED}}(\omega_0 + \Delta) A_{\text{MD}}(\omega_0 - \Delta) - A_{\text{ED}}(\omega_0 - \Delta) A_{\text{MD}}(\omega_0 + \Delta)}, \tag{S16}
\]

\[
\tilde{\rho}_{s,p}^{\text{MD}}(\omega_0, k_{\parallel}) = \frac{C_1 N_{s,p}(\omega_0 + \Delta, k_{\parallel}) A_{\text{ED}}(\omega_0 - \Delta) - N_{s,p}(\omega_0 - \Delta, k_{\parallel}) A_{\text{ED}}(\omega_0 + \Delta)}{C_2 A_{\text{MD}}(\omega_0 + \Delta) A_{\text{ED}}(\omega_0 - \Delta) - A_{\text{MD}}(\omega_0 - \Delta) A_{\text{ED}}(\omega_0 + \Delta)}, \tag{S17}
\]

where \( C_1 \) is the proportionality constant from the initial measurement of the intrinsic rates in a known environment, and \( C_2 \) is the proportionality constant from the second measurement of emission in an unknown environment.

This technique can also be extended to simultaneously fit three or more cross-sections acquired at closely-spaced frequencies \( (\omega) \) to reduce the effects of noise and to assess confidence intervals. For this purpose, Fig. 3e in the main text was produced using a least squares routine to independently fit the following system of linear equations for each momentum value \( (k_{\parallel}) \) over the 1 nm range from 580.6 - 581.6 nm centered about \( \omega_0 = 581.1 \) nm:

\[
\frac{C_2}{C_1} \begin{bmatrix} A_{\text{ED}}(\omega) & A_{\text{MD}}(\omega) \end{bmatrix} \begin{bmatrix} \tilde{\rho}_{s,p}^{\text{ED}}(\omega_0) \\ \tilde{\rho}_{s,p}^{\text{MD}}(\omega_0) \end{bmatrix} = N_{s,p}(\omega) \tag{S18}
\]
Supplementary References