SUPPORTING INFORMATION

Energy Transfer Mechanism and Quantitative Modeling of Rate from an Antenna to a Lanthanide Ion

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S9 UNITS AND CONVERSIONS USED IN THIS WORK

S10 REFERENCES

### S1. EXPERIMENTAL

| Wavenumber (cm$^{-1}$) | Ref. S1 | Ref. S2 | This work | Calc. DFT |
|------------------------|---------|---------|-----------|-----------|
| 1592                   | 1588    | 1583    | 1590      |           |
| 1508                   | 1514    | 1514    | 1471      |           |
| 1499                   | --      |         | 1505      |           |
| 1397                   | 1412    | 1409    | 1406      |           |
| 1346                   | 1359    | 1353    | 1352      |           |
| 1289                   | 1305    | 1285    | 1281      |           |
| 1245                   | 1253    | 1249    | 1260      |           |
| 1220                   | 1232    | 1231    | 1223      |           |
| 1196                   | 1196    | --      |           |           |
| 1179                   | --      | 1182    | 1187      |           |
| 1134                   | 1144    | 1131    |           |           |
| 1072                   | 1084    | 1082    | 1098      |           |
| 1054                   | 1064    | 1061    | 1063      |           |
Table S1. Reported bands in the infrared spectrum of \textbf{Eu(TTA)$_3$(H$_2$O)$_2$}. Ref. S1: a list of bands is given with wavelengths in microns; Ref. S2: scanned from the spectrum in the Supporting Information of Ref. S2. Calc. DFT: gas phase, MWB52 PBE0/D3BJ/def2-TZVP level.

| 1033 | 1036 |
|------|------|
| 1028 | --   |
| 1004 | 1012 |
| 927  | 933  |
| 921  | --   |
| 856  | 860  |
| 827  | 792  |
| 782  | --   |
| 762  | 769  |
| 746  | 749  |
| 729  | 726  |
| 707  | 715  |
| 689  | 694  |
| 677  | 681  |

Figure S1. Thermogravimetric analysis results for \textbf{Eu(TTA)$_3$(H$_2$O)$_2$} using atmospheres of (a) nitrogen and (b) air. The initial loss of mass commences at 100 °C, up to 120-130 °C, and corresponds to the loss of two water molecules. The X-Ray diffractogram of \textbf{Eu(TTA)$_3$(H$_2$O)$_2$} is given in Ref. S3. Attempts in the present study to employ X-ray diffraction led to sample decomposition.
## S2. COMPUTATION OF MOLECULAR STRUCTURE

| Atom | Distance (Å) | DFT<sup>a</sup> | DFT<sup>b</sup> | DFT<sup>c</sup> | Triclinic Structure<sup>d</sup> | Monoclinic Structure<sup>e</sup> |
|------|--------------|-----------------|-----------------|-----------------|------------------------|------------------------|
| O8(w) | 2.499        | 2.542           | 2.506           | 2.424           | 2.507                  |                         |
| O7(w) | 2.619        | 2.612           | 2.586           | 2.408           | 2.545                  |                         |
| O6    | 2.384        | 2.424           | 2.366           | 2.419           | 2.466                  |                         |
| O5    | 2.358        | 2.363           | 2.397           | 2.405           | 2.384                  |                         |
| O4    | 2.386        | 2.394           | 2.421           | 2.330           | 2.496                  |                         |
| O3    | 2.368        | 2.402           | 2.369           | 2.380           | 2.381                  |                         |
| O2    | 2.396        | 2.371           | 2.445           | 2.369           | 2.388                  |                         |
| O1    | 2.379        | 2.393           | 2.377           | 2.389           | 2.507                  |                         |

Table S2. Bond distances in the first coordination sphere of Eu in Eu(TTA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>

<sup>a</sup>MWB52-PBE0/D3BJ/def2-TZVP; <sup>b</sup>including CPCM(toluene); <sup>c</sup>Ref. S4, CHCl<sub>3</sub>, BP86/def2-TZVP.

## S3. SINGLET ENERGY AND OSCILLATOR STRENGTH

We envisage that after ultraviolet excitation, rapid intersystem crossing occurs from the higher singlet states to the lowest one, which then can undergo intersystem crossing and/or direct ET to Eu<sup>3+</sup>. The transfer occurs from the S<sub>1</sub> – S<sub>0</sub> zero phonon line (ZPL). This energy may be calculated by the ΔSCF method and is generally at several thousand cm<sup>-1</sup> lower than that calculated for the corresponding vertical transition by TD-DFT.<sup>55</sup> The room temperature spectra emission spectra of HTTA, La(TTA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> and Eu(TTA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> are too broad for estimation of the ZPL energy, Figure S2(a), but it is readily assigned at 25410 cm<sup>-1</sup> at 77 K, Figure S2(b).

The room temperature absorption spectra of Eu(TTA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> in toluene at different concentrations are displayed in Figure S2(c) and are similar to the literature spectra. The singlet oscillator strength can be calculated from absorption, Eq. (2-6) or emission, Eq. (1) measurements. The absorption spectrum of Eu(TTA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> in acetonitrile has been reported<sup>51,52,56</sup> and our deconvolution of the first broad absorption band in Ref. S7 into two Gaussians gives the oscillator strength of 0.05 for the lower energy one, using Eq. 5. However, our calculations show that there are not two, but about 10 different singlet states in this spectral region and fitting our experimental spectra with multiple Gaussians is not accurate. The calculated TD-DFT oscillator strengths of the lowest singlet state of Eu(TTA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> in toluene
(vertical transition energy $24871 \text{ cm}^{-1}$, 402 nm) and in the gas phase (vertical transition energy $29867 \text{ cm}^{-1}$, 335 nm) are 0.0048 and 0.0083, respectively.

Figure S2e shows the room temperature excitation spectra of Eu(TTA)$_3$(H$_2$O)$_2$ in toluene and in the solid state. The singlet absorption band is red-shifted and broadened for the solid, where Eu$^{3+}$ transitions are observed. The packing of Eu(TTA)$_3$(H$_2$O)$_2$ units increases by a magnitude of $2.2 \times 10^5$ from 10 $\mu$M concentration in a solvent to the solid and this has been taken to indicate greater spin-orbit coupling and hence faster intersystem crossing to the triplet state. The appearance of the europium absorption bands indicates greater competition of internal Eu$^{3+}$ excitation with the antenna ET in the solid state, and may involve $4f^6 - 4f^6$ cross-relaxation processes in the solid state. The measured ratio of the integrated areas (${^7}F_0 \rightarrow {^5}D_0)/({^7}F_0 \rightarrow {^5}D_1$) [at, in cm$^{-1}$: 21552/19052] in the excitation spectrum of solid Eu(TTA)$_3$(H$_2$O)$_2$ at room temperature in Figure S2e is 110, which is far from the nearly equal ratios from the absorption spectra. This may indicate that $^5D_0$ is more favorably populated in the solid state by excitation into $^5D_2$, rather than $^5D_1$, due to the cross-relaxation: $^5D_2 + {^7}F_0 \rightarrow ^5D_0 + {^7}F_5$. There is a first-order $J$-selection rule prohibiting $^5D_1 \rightarrow ^5D_0$ vibrational relaxation, mentioned below.

The singlet emission of Eu(TTA)$_3$(H$_2$O)$_2$ is totally quenched at room temperature when it is dissolved in toluene, but a very weak band with maximum at ~425 nm is observed for the solid (Figure S2a). This could be due to dissociation, but if it corresponds to Eu(TTA)$_3$(H$_2$O)$_2$ singlet emission, then the singlet ET/intersystem crossing rate is of the same order as the singlet lifetime for Eu(TTA)$_3$(H$_2$O)$_2$ in the solid state at room temperature. The singlet emission of HTTA, with maximum at 441 nm, exhibits monoexponential decay with the lifetime of 1.3 ns at room temperature and 5.1 ns at 77 K (Figure S2d). The corresponding lifetime for La(TTA)$_3$(H$_2$O)$_2$ at 77 K is 3.5±0.3 ns (Figure S2f). From Eq. 1, a 5 ns radiative lifetime is equivalent to an oscillator strength of about 0.19, whereas a 20 ns radiative lifetime would give $P_f \sim 0.05$. In the case of La(TTA)$_3$(H$_2$O)$_2$, a 20 ns radiative lifetime would represent a quantum efficiency of 18%.

S5
Figure S2. (a) Room temperature emission spectra of HTTA and Eu(TTA)$_3$(H$_2$O)$_2$ in the solid state using the excitation wavelengths indicated. (b) 77 K emission spectra of La(TTA)$_3$(H$_2$O)$_2$ (blue) and HTTA (magenta) at 10 µM concentration in toluene using 300 nm excitation; excitation spectra of 550 nm (green) and 580 nm (red) emission of solid La(TTA)$_3$(H$_2$O)$_2$. The S$_1$ – S$_0$ zero phonon line is indicated as 0-0 with the most prominent vibronic transitions involving the C=O stretching vibration of 1660±20 cm$^{-1}$ marked as 1 and 1’. (c) Concentration dependence of room temperature absorption spectrum of Eu(TTA)$_3$(H$_2$O)$_2$ in toluene. (d) Singlet emission decay of solid HTTA at 77 K. The laser prompt is shown. (e) Room temperature excitation spectrum of (red) 610 nm emission of solid Eu(TTA)$_3$(H$_2$O)$_2$. The inset shows an ordinate scale expansion; (blue) Room temperature excitation spectrum of 613 nm emission of 50 µM Eu(TTA)$_3$(H$_2$O)$_2$ in toluene; (magenta) 77 K excitation spectrum of 613 nm emission of 10 µM Eu(TTA)$_3$(H$_2$O)$_2$ in toluene. (f) Singlet emission decay of solid La(TTA)$_3$(H$_2$O)$_2$ at 77 K. (g) Calculated CASSCF-NEVPT2 absorption spectra of Eu(TTA)$_3$(H$_2$O)$_2$ in the gas phase using different active spaces, as
indicated. The spectra show bands in the region of 310 nm and 340-350 nm but the relative intensity changes with choice of active space.

| Energy Level | \( \text{Y}_2\text{O}_3:\text{Eu}^{2+} \) bc | \( \text{EuCl}_3.6\text{H}_2\text{O}^{510} \) Energy range (no. of bands) | \( \text{Cs}_2\text{NaEuCl}_6^{511} \) Energy range (no. of bands) | \( \text{LaF}_3:\text{Eu}^{512} \) bc | \( \text{Eu(TTA)}_3(\text{H}_2\text{O})_2 \) |
|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( ^5\text{D}_0 \) | 17216 | 17248 (1) | 17208 (1) | 17293 | 17303 |
| \( ^5\text{D}_1 \) | 18959 | 18993-19018 (3) | 18961 (1) | 19027 | 19052 |
| \( ^5\text{D}_2 \) | 21421 | 21446-21514 (5) | 21385-21495 (2) | 21483 | 21552 |
| \( ^5\text{D}_3 \) | 24265 | 24537-(24399) (7) | 24261-24370 (3) | 24355 | |
| \( ^5\text{L}_6 \) | 24950 | 24988-25327 (13) | 24761-25345 (6) | 25325 | 25146 |
| \( ^5\text{D}_4, ^5\text{L}_9 \) | 27585-27690 (9) | | | | |
| \( ^5\text{L}_7 \) | | 25893-26099 (4) | 26357 | | |
| \( ^5\text{G}_2 \) | | 26162-26175 (2) | 26392 | | |
| \( ^5\text{G}_3 \) | | 26216 (1) | 26622 | | |
| \( ^5\text{L}_7 \) | | 26240 (1) | | | |
| \( ^5\text{G}_3 \) | | 26338 (1) | | | |
| \( ^5\text{G}_4 \) | | 26339 (1) | 26735 | | |
| \( ^5\text{L}_7 \) | | 26345 (1) | | | |
| \( ^5\text{G}_4 \) | | 26424 (1) | | | |

Table S3. Selected europium energy levels in materials. Values are given in cm\(^{-1}\). bc barycenter. The Eu\(^{3+}\) states above 26000 cm\(^{-1}\) are of much more mixed parentage.

**S4. OSCILLATOR STRENGTHS**

Some values of oscillator strength for Eu\(^{3+}\) transitions are listed in Table S4, taken from the literature and the present study.
Figure S3. Room temperature absorption spectrum of EuCl$_3$·6H$_2$O dissolved in water.

| System       | State       | Transition | Eq | Osc. Str. Abs. | Osc. Str. Corr.$^a$ | Ref. | Comments        |
|--------------|-------------|------------|----|----------------|----------------------|------|-----------------|
| EuCl$_3$     | aq./band max | $^7$F$_0$ → $^5$D$_0$ | 5  | 1.66E-10       | 3.19E-10             |      |                 |
|              |             | $^7$F$_0$ → $^5$D$_1$ | 5  | 1.41E-8        | 2.71E-8              |      |                 |
|              |             | $^7$F$_0$ → $^5$D$_2$ | 5  | 1.36E-8        | 2.61E-8              |      |                 |
|              |             | $^7$F$_0$ → $^5$D$_3$ | 5  | 2.74E-8        | 5.27E-8              |      |                 |
|              |             | $^7$F$_0$ → $^5$L$_6$ | 5  | 1.82E-6        | 3.50E-6              |      |                 |
|              |             | $^7$F$_1$ → $^5$G$_2$ | 5  | 3.07E-7        | 5.90E-7              |      |                 |
|              |             | $^7$F$_1$ → $^5$D$_0$ | 5  | 8.15E-9        | 1.70E-8              |      |                 |
| EuCl$_3$·6H$_2$O | Solid/bands | $^7$F$_0$ → $^5$D$_0$ | 2.2E-9 |      | S13 ED             |      |                 |
|              |             | $^7$F$_0$ → $^5$D$_1$ | 1.25E-8 |      | S13 Mainly MD; 7.2E-10 ED |      |                 |
|              |             | $^7$F$_0$ → $^5$D$_2$ | 1.44E-8 |      | S13 ED             |      |                 |
| Eu(TTA)$_3$(H$_2$O)$_2$ | Toluene | $^7$F$_0$ → $^5$D$_0$ | 2.2E-9 |      | S13 | ED |
|                | Transitions          | Oscillator Strengths | References |
|----------------|----------------------|----------------------|------------|
| **Eu(DBM)(H₂O)** | \( ^{7}F_{0} \rightarrow ^{5}D_{2} \) | 5 \( \times 10^{-6} \) | 1.32E-6   |
|                |                      |                      | 2.54E-6   |
|                | \( ^{7}F_{0} \rightarrow ^{5}D_{0} \) | 2.6E-8               | S14        |
|                |                      | 7.9E-8               |            |
|                | \( ^{7}F_{0} \rightarrow ^{5}D_{1} \) | 1.2E-7               |            |
|                | \( ^{7}F_{0} \rightarrow ^{5}D_{2} \) | 3.91E-6              |            |
|                | \( ^{7}F_{1} \rightarrow ^{5}D_{0} \) | 8 \( \times 10^{-6} \) | S15        |
|                | \( ^{7}F_{1} \rightarrow ^{5}D_{1} \) | \((8.5 \pm 0.3)\)E-6 | S14        |

**Na₃[Eu(ODA)₃] 2NaClO₄ 6H₂O**

|                | Transitions          | Oscillator Strengths | References |
|----------------|----------------------|----------------------|------------|
|                | \( ^{7}F_{1} \rightarrow ^{5}D_{1} \) | \((8.5 \pm 0.3)\)E-6 | S14        |
|                | \( ^{7}F_{0} \rightarrow ^{5}D_{1} \) | \((8.5 \pm 0.3)\)E-6 | S16        |

Table S4. Measured oscillator strengths of Eu³⁺ transitions for various systems. Data from the present work or given references. DBM dibenzylmethanido. ODA oxydiacetato. The values are corrected for the population of the \( ^{7}F_{0} \) and \( ^{7}F_{1} \) states, assuming a barycenter of 380 cm⁻¹.

The intensity of these bands can arise from several mechanisms. The \( ^{7}F_{0} \) - \( ^{5}D_{1} \) and \( ^{7}F_{1} \) - \( ^{5}D_{0} \) transitions are mainly of magnetic dipole (MD) character. The \( ^{7}F_{0} \) - \( ^{5}D_{0} \) transition is forbidden under Judd-Ofelt theory, but the breakdown of the closure approximation, \( J \)-mixing and the Wybourne-Downer process enable this transition to gain intensity. Furthermore, it can gain intensity via crystal strain to give coincident defect site bands. We measured the oscillator strength for this transition of Eu³⁺ in aqueous EuCl₃ (Figure S3) to be \( 1.7 \times 10^{-10} \), whereas Hellwege and Kahle gave the magnitude of \( 2.2 \times 10^{-9} \) and Ferrier et al. gave the value \( 1.3 \times 10^{-9} \) for \( Y_{2}SiO_{5}:Eu^{3+} \).

The strongest Eu³⁺ transition in our region of interest is \( ^{7}F_{0} \) - \( ^{5}L_{6} \), with the oscillator strength of the order \( 10^{-6} \), which is mainly of ED character. Electric dipole transitions gain intensity by both static and dynamic coupling mechanisms, in addition to the cross-terms of these. The ED intensities depend upon the system geometry, charges and dipolar polarizabilities.

**S5. THE SPECTRAL OVERLAP INTEGRAL**

This integral is of the form:

\[
SOI = \int_{-\infty}^{\infty} f_D(E) f_A(E) dE
\]  

(S1)
where the \( f(E) \) are the normalized donor emission and acceptor absorption spectra on an energy scale. In our case, the antenna donor (D) has a broad emission spectrum, and the lanthanide acceptor (A) spectrum is a sharp band.

For an example, we model these by two Gaussian functions, \( y(D) \) and \( y(A) \), where \( y \) is given by:

\[
y = y_0 + \left[ A' \exp \left( \frac{-4\ln(2)(E-E_c)^2}{w^2} \right) \right] / \left[ w \sqrt{\frac{\pi}{4\ln(2)}} \right] \]

(S2)

Here, \( y_0 \) is the lower \( y \) value; \( A' \) is the peak area; \( E_c \) is the peak center (unit eV); \( w \) = FWHM;

The two Gaussian functions each have \( A' = 1 \), \( y_0 = 0 \):

For D, simulating singlet emission, \( H = 0.6 \) eV, \( E_c = 2.77 \) eV, and for A, simulating \(^5\)D\(_0\) absorption, \( H = 0.006 \) eV, \( E_c = 2.14 \) eV. Each simulation in Origin employed 20000 data points. Then:

\[
D := 1.566300*\exp(-7.707470*(E-2.770000)^2)
\]

\[
A := 156.632000*\exp(-77074.70*(E-2.140000)^2)
\]

From Maple 2021:\(^{518}\)

\[
\int_{-\infty}^{\infty} f(D)f(A) \, dE = 0.073669 \text{ eV}^{-1}
\]

The integral gives the same result as long as the interval extends over the acceptor profile. Plotting the curves gives Figure S4:

![Figure S4. Overlap of two Gaussians. The singlet donor emission is shown in the inset on an expanded ordinate scale.](image)

where the donor is shown on an expanded ordinate scale in the inset. The spectral overlap area was calculated from the columns \( y(D) \) and \( y(A) \) in Origin \(^9\)\(^{519}\) with rows having the same abscissa \( E \):

\[
\text{area} = \text{sum}(y(D)[i]*y(A)[j]*(E[i+1] - E[i]))
\]

(S3)

and gave the result indicated in the graph, very close to the calculated integral. On the other hand, if we just consider the region where the curves overlap, we have Figure S5, where the area is 47 times smaller.
Figure S5. Spectral overlap of area under two Gaussians.
Figure S6. Spectral overlap diagrams. (a) Gd(TTA)$_3$(H$_2$O)$_2$ solid-state phosphorescence T$_1$ → S$_0$ and Eu(TTA)$_3$(H$_2$O)$_2$ solid state 355 nm excited emission spectrum at room temperature. (b) Singlet emission of solid HTTA and Eu(TTA)$_3$(H$_2$O)$_2$ solid state 355 nm excited emission spectrum at room temperature. (c) Singlet emission of solid Gd(TTA)$_3$(H$_2$O)$_2$ and emission spectrum of solid Eu(TTA)$_3$(H$_2$O)$_2$ at room temperature.
temperature. (d) Singlet emission of solid Eu(TTA)$_3$(H$_2$O)$_2$ and absorption spectrum of solid Eu(TTA)$_3$(H$_2$O)$_2$. (e), (f) Singlet emission of solid HTTA and absorption spectrum of aqueous EuCl$_3$.6H$_2$O. (g) Singlet emission of solid Eu(TTA)$_3$(H$_2$O)$_2$ and excitation spectrum of solid Eu(TTA)$_3$(H$_2$O)$_2$ at room temperature. (h) Singlet emission of solid Eu(TTA)$_3$(H$_2$O)$_2$ and absorption spectrum of solid Eu(TTA)$_3$(H$_2$O)$_2$. (i), (j) Singlet emission of solid Eu(TTA)$_3$(H$_2$O)$_2$ and absorption spectrum of aqueous EuCl$_3$.6H$_2$O. (k) Triplet emission of solid Eu(TTA)$_3$(H$_2$O)$_2$ and emission spectrum of 10 µM Eu(TTA)$_3$(H$_2$O)$_2$ in toluene. (l) Singlet emission of solid Eu(TTA)$_3$(H$_2$O)$_2$ and emission spectrum of 10 µM Eu(TTA)$_3$(H$_2$O)$_2$ in toluene. In k, l, the populations of $^7$F$_{1/2}$ crystal field states have been adjusted to change from emission to absorption.

S7. RATE EQUATION MODEL

Initial parameter values. The value of Q is arbitrary$^{520}$ and its variation within a reasonable range does not affect the conclusions herein. Phosphorescence is quenched at room temperature. The value of parameter b indicates a fluorescence lifetime of 3.3 ns. The intersystem crossing rate (f) in lanthanide complexes is generally taken to be in the range of 10$^6$-10$^9$ s$^{-1}$. The larger value is taken because the fluorescence is (mostly?) quenched. We take the room temperature value$^{521}$ of 0.2 ms for the $^5$D$_0$ lifetime, and the value 0.256 ms at 10 K (Fig. 3a, Ref. S21). The singlet ET rate is the sum of calculated values for $S_1 \rightarrow DJ$ (g), $^5$D$_1$ (k) or $^5$D$_0$ (m) with $^7$F$_0$, $^7$F$_1$ at 300 K, and only for $^7$F$_0$ at 10 K. The parameter values for g, k, m are similar to those calculated in Table 3 of the manuscript. The triplet ET rate is the sum of $T_1 \rightarrow ^5$D$_1$ (n) or $^5$D$_0$ (p) with $^7$F$_0$, $^7$F$_1$ at 300 K, and only for $^7$F$_0$ at 10 K. The $^5$D$_1$ risetime at 300 K or 10 K in Fig. 4b of Ref. S21 was used to calculate rate constant n, considering the level occupations, overlap integrals and degeneracies of $^7$F$_0$, $^7$F$_1$. Also, we have employed the trial values of n = 1E8 s$^{-1}$ and 1E9 s$^{-1}$, even reducing g = 1E8 s$^{-1}$, but then the $^5$D$_1$ risetimes are too fast. This puts an upper limit to the exchange contribution to parameter n. The parameter value p is not known but is expected to be smaller than n. The internal conversion parameter s was initially set at 10$^8$ s$^{-1}$. The gap Eu$^{3+}$ ($^5$D$_2$ - $^5$D$_1$) is 2500 cm$^{-1}$, which can be spanned by two phonons. However, the most effective nonradiative process cannot just be estimated from the energy gap and the maximum phonon frequency.$^{522}$ The energy gap for Pr$^{3+}$ ($^3$P$_0$ - $^1$D$_2$) is 2600-2700 in M$_2$O$_5$:Pr$^{3+}$ (M = Y, Lu) with the room temperature multiphonon relaxation rate >10$^7$ s$^{-1}$.$^{523}$ Gaps between the energy levels of LiYF$_4$:Nd$^{3+}$ of 938-1649 cm$^{-1}$ are associated with nonradiative decay rates of 10$^{6}$-10$^9$ s$^{-1}$.$^{522}$ The parameters d and u were adjusted to give the $^5$D$_1$ lifetimes at 300 K and 10 K. The fact that the risetime of $^5$D$_0$ equals the lifetime of $^5$D$_1$ (Fig. 5, Ref. S21) means that the radiative lifetime of $^5$D$_1$ is orders of magnitude longer than the nonradiative relaxation rate. The $^5$D$_1$ - $^5$D$_0$ nonradiative decay is a special case where J = 1 $\rightarrow$ J = 0 selection rule limits the nonradiative relaxation rate, just as for Pr$^{3+}$ ($^3$P$_1$ - $^3$P$_0$) with the gap of 621 cm$^{-1}$ but with the slow rate of 3.33x10$^5$ s$^{-1}$.$^{524}$ The change in nonradiative relaxation rate of ($^5$D$_1$ - $^5$D$_0$) from 10 K to 300 K is estimated to be an order of magnitude.$^{525}$

Zero energy transfer scenarios at 300 K and 10 K. The zero singlet energy transfer at 300 K gives the following results using a 5 ns pulse.
Figure S7. Zero singlet ET. 300 K energy level time profiles following a 5 ns pulse with the parameters in Table 3, columns 3 and 7, except with k, m and g set equal to zero. (a) $^5D_0$; (b) $^5D_1$; (c) $S_1$; (d) $S_0$; (e) $T_1$; (f) $F_0$. The population of DJ is zero. Black curves are calculated by Maple 2021 and red curves are fitted by Origin 9 mono- or bi-exponential functions, with lifetimes as indicated. In these and in the following figures, the Counts for $F_0$ and $S_0$ are 0.99999999 or similar.
Zero singlet energy transfer scenario at 10 K. The results are plotted in Figure S8.

Figure S8. Zero singlet ET, 10 K. This calculation uses the same parameters as in Table 3 columns 4 and 8, with the triplet state energy transfer only involving $^7F_0$, not $^7F_1$. (a) $^5D_0$; (b) $^5D_1$; (c) $T_1$. Parameters $k$, $m$ and $g$ are set equal to zero. Again, a 5 ns pulse was used.

Figure S9. Zero singlet ET, 10 K. This calculation uses the same parameters as in Table 3 columns 4 and 8, and Figure S8, except $f = 10^8$ s$^{-1}$. As above a 5 ns pulse was used. (a) $^5D_0$; (b) $^5D_1$; (c) $T_1$. The triplet state energy transfer only involves $^7F_0$, not $^7F_1$. Black curves are calculated by Maple 2021 and red curves are fitted by Origin 9 mono- or bi-exponential functions, with lifetimes as indicated.

Figure S10. Zero singlet ET, 10 K. (a) $^5D_1$; (b) $T_1$. This calculation uses the same parameters as in Table 3 column 4 and Figure S8, except $f = 10^8$ s$^{-1}$, $a = 10^6$ s$^{-1}$. As in Figures S8 and S9, parameters $k$, $m$ and $g$ are set equal to zero. A 5 ns pulse was used. The triplet state energy transfer only involves $^7F_0$, not $^7F_1$. Black
curves are calculated by Maple 2021 and red curves are fitted by Origin 9 mono- or bi-exponential functions, with lifetimes as indicated.

Zero triplet energy transfer scenario, 300 K and 10 K
Figure S11. Zero Triplet ET. 300 K energy level time profiles with the parameters in Table 3, columns 3 and 7, except with n and p set equal to zero. A 5 ns pulse was used. (a) $^5D_0$; (b) $^5D_1$; (c) DJ; (d) $^7F_0$; (e) $S_0$; (f) $S_1$; (g) $T_1$. Black curves are calculated by Maple 2021 and red curves fitted by Origin mono- or bi-exponential functions with lifetimes as indicated. The differential equations were solved by the Rosenbrock (labeled (ii)) or Runge-Kutta-Fehlberg (rkf45) (labeled (iii)) algorithm with automatic error estimation using rules of order 4 and 5, as indicated. The Rosenbrock method is more stable but gives an artifact (for example at 3.5 $\mu$s for $^5D_0$) which is not present in the rkf45 method.
Figure S12. Zero Triplet ET. 10 K energy level time profiles with the parameters in Table 3, columns 4 and 8, except with n and p set equal to zero. A 5 ns pulse was used. (a) \(^5\)D\(_0\); (b) \(^5\)D\(_1\); (c) \(T_1\), ns range; (d) \(T_1\), ms range; (e) DJ. Note the different ranges for \(T_1\) in (c), (d). Black curves are calculated by Maple 2021 and red curves are fitted by Origin 9 mono- or bi-exponential functions, with lifetimes as indicated.
Figure S13. Zero Triplet ET. 10 K energy level time profiles with the parameters in Table 3, columns 4 and 8, except with n and p set equal to zero and s = 1E7 s⁻¹. A 5 ns pulse was used. (a) \( ^5D_0 \); (b) \( ^5D_1 \); (c) \( T_1 \), ns range; (d) \( T_1 \), ms range; (e) DJ. Note the different ranges for \( T_1 \) in (c), (d). Black curves are calculated by Maple 2021 and red curves are fitted by Origin 9 mono- or bi-exponential functions, with lifetimes as indicated.
Singlet and triplet energy transfer.

Figure S14. Calculated 10 K time profiles of levels using the Rosenbrock method, following a 5 ns pulse. (a) $^5D_0$; (b) $^5D_1$; (c) DJ; (d) $T_1$; (e) $S_0$; (f) $S_1$; (g) $^7F_0$. The parameters are in columns 4 and 8 of Table 3 (black
S8. Calculations Using the Model of Malta

A. Comments upon the model. There are some assumptions in Malta’s model - necessary to avoid complicated expressions with parameters unrelated to experimental data and some restrictions on the usage of parameters in the LUMPAC\textsuperscript{26} and JOYSpectra\textsuperscript{27} software. The model employs selection rules based upon \( J \)-multiplet terms. By contrast, note that the crystal field levels of each multiplet often have mixed parentage and they are split at a low site symmetry over a range of energy. For example, even in a highly symmetric octahedral environment of Eu\textsuperscript{3+} in \( \text{Cs}_2\text{NaEuCl}_6 \), the \( ^5\!L_6 \) multiplet is split by 584 cm\textsuperscript{-1}.

In the theory of Malta, and subsequently in LUMPAC and JOYSpectra, the spectral overlap integral has been represented by \( F \), in units of erg\textsuperscript{-1}:

\[
F = \frac{1}{\hbar \gamma_L} \frac{\ln 2}{\pi} e^{- \left( \frac{\Delta}{\hbar \gamma_L} \right)^2 \ln 2}
\]

where \( \gamma_L \) is the full width at half maximum (FWHM) of the broad emission band (rad s\textsuperscript{-1}), \( \hbar \) is the reduced Planck constant and \( \Delta \) (erg) is the energy difference between the band maxima.

For example, as above in Section S6, \( \gamma_L = 0.6 \text{ eV} = 0.6 \times 8065.5439 \text{ cm}^{-1} = 4839.326 \text{ cm}^{-1} \);

\[
\Delta = 2.77 - 2.14 = 0.63 \text{ eV} = 5081.293 \text{ cm}^{-1} \]

\[
F = \frac{1}{1.054571726 \times 10^{-34} \times 4839.326 \times 2.99792458 \times 10^{10} \times 2 \times \pi \frac{0.693147}{3.141593}}^{0.5} \times \exp \left( - \frac{5081.293}{4839.326} \frac{0.693147}{0.693147} \right) = 2.275572 \times 10^{18} \text{ J}^{-1}
\]

This value is 4.96 times larger than that calculated from Maple 2021 above. The Table S5 shows calculated values of the overlap integral using direct integration with Maple 2021 and using the formula S4 for \( F \). The ratio of the values obtained is less than 5 for values of \( \Delta \) (ligand energy – Eu\textsuperscript{3+} energy) \( \sim 0.7 \) eV \( \sim 5646 \text{ cm}^{-1} \) but increases to a factor near 5000 for values of \( \Delta \) over 10000 cm\textsuperscript{-1}. In practice, the singlet emission band maximum is usually lower than 3 eV but both LUMPAC\textsuperscript{26} and JOYSpectra\textsuperscript{27} use the energy of the vertical transition (and not the zero phonon line) in the absorption spectrum. In this case, the singlet state peak maximum would be about 0.58 eV (4700 cm\textsuperscript{-1}) too high in the present case for Eu(TTA)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{2}, leading to considerable error in \( F \).

| Ligand energy\textsuperscript{a} | Spectral overlap integral (eV\textsuperscript{-1}) | Ratio A/B |
|---------------------|-----------------------------|----------|
| eV/cm\textsuperscript{-1} | (A) Direct calculation | (B) Using formula S4 |
| 2.3 | 18551 | 1.2855 | 0.7452 | 1.7 |
Table S5. Calculation of spectral overlap integral using direct integration with Maple 2021 and with Eq. S4 for \( F \). The ligand band maximum with FWHM of 0.6 eV is varied in energy whilst keeping the Eu\(^{3+} \) level constant at 2.14 eV, with FWHM of 0.006 eV. \(^a\)This is the band maximum, not the zero phonon line energy. Note that the value of \( \gamma_L \) is fixed in calculations of LUMPAC at 3250 cm\(^{-1} \) and in JOYSpectra it can be varied.

In fact, in our manuscript, the spectral overlap integrals are all small, in the narrow range from 0.17 eV\(^{-1} \) to 2.3 eV\(^{-1} \) (column 3, Table 2). The values calculated by Eq. S4 for \( F \) by using the band maxima for donor emission and acceptor absorption are within an order of magnitude except for singlet to \( ^5\text{D}_0 \) ET. Note however that both LUMPAC and JOYSpectra do not use donor emission band maxima but utilize the donor absorption band maxima for calculation and this may be about 8000 cm\(^{-1} \) higher in energy than the emission band maximum. The results then differ considerably.

**B. Calculations using LUMPAC and JOYSpectra.** The software LUMPAC\(^{526} \) utilizes the europium room temperature emission spectrum, the \( ^5\text{D}_0 \) emission lifetime, and an input file with the molecular structure of the complex. The output gives ET rates from the ligand singlet and triplet states to various Eu\(^{3+} \) states. It is described in a tutorial\(^{528} \) and in Ref. 520.

Some points concerning the program are that:

(i) the ligand singlet transition dipole strength is fixed at 10\(^{-35} \) esu\(^2 \) cm\(^2 \).

(ii) the donor-acceptor spectral overlap function \( F \) uses the value of ligand full width at half-maximum (FWHM) equal to 3250 cm\(^{-1} \) (0.40 eV).

(iii) LUMPAC considers a thermal population of 0.6 and 0.3 for \( ^7\text{F}_0 \) and \( ^7\text{F}_1 \), respectively, so that ET for the \( \text{T}_1 - ^5\text{D}_0 \) channel corresponds to the excitation \( ^7\text{F}_1 \rightarrow ^5\text{D}_0 \).

(iv) The energy of the singlet vertical absorption transition (instead of emission) is employed in the calculation of \( F \).

(v) The Eu\(^{3+} \) energy levels and matrix elements are taken from the study of LaF\(_3\):Eu\(^{3+} \) whereas the coordination sphere of Eu\(^{3+} \) in organic complexes usually comprises nitrogen and/or oxygen atoms.

(vi) The calculation of triplet and singlet state energies is fast using INDO/S-CIS or TD-DFT in ORCA but the results are inaccurate.

(vii) The formulation of the rate equations is not the same as in herein.
(viii) The model of Malta includes the contribution from exchange interaction, but the relevant exchange integral is approximated by that of the dipole moment operator. In particular, the same magnitude is taken for singlet or triplet donors.

When calculating the ET rate from the antenna singlet state to Eu$^{3+}$, both LUMPAC and JOYSpectra require the energy of the $S_1 \rightarrow S_0$ band maximum. The value in LUMPAC is taken from the energy calculation by ZINDO/S for the singlet state with highest oscillator strength, although the state can be changed by manually modifying the file. The value in JOYSpectra may be entered but for the example file of Eu(TTA)$_3$(H$_2$O)$_2$ it has been set at 29900 cm$^{-1}$ (334 nm). This energy is far above the $S_1$ zero phonon line from which transfer occurs.

The more recent JOYSpectra software overcomes some of these points, in particular in providing the opportunity to adjust the FWHM in the calculation of $F$. The example input file for Eu(TTA)$_3$(H$_2$O)$_2$ uses $S_1$ and $T_1$ energies 29900 and 20300 cm$^{-1}$, respectively, which lead to errors since the values are inaccurate. In particular, ET processes are listed for Eu$^{3+}$ levels which are higher in energy than the donor singlet state.

The ET rate calculation was carried out using the coordinates given for Eu(TTA)$_3$(H$_2$O)$_2$ in JOYSpectra. The ORCA energy level calculation in LUMPAC utilizes ZINDO/S and it gave triplet energies commencing at 12755 cm$^{-1}$, which is far too low in energy. The normal (auto) calculations in the software choose singlet states which are far above normal excitation wavelengths so that the calculations do not reflect physical situations. For the calculation of ET rates in our case, Table S6, the calculated fourth triplet (19961 cm$^{-1}$) and lowest singlet state (28964 cm$^{-1}$) were chosen as the ligand states in LUMPAC. In JOYSpectra, the ligand states were chosen at $S_1$ 25000 cm$^{-1}$, $T_1$ 19802 cm$^{-1}$. Our calculations for the ET rates of Eu(TTA)$_3$(H$_2$O)$_2$ using these energies in the software LUMPAC and JOYSpectra are given in Table S6. The overwhelming contribution comes from exchange because of the approximation made for its matrix element.$^{330,331}$

| Ligand states | Eu$^{3+}$ states | Overall ET rate (s$^{-1}$) |
|---------------|-----------------|--------------------------|
|               | LUMPAC $\gamma_1$ 3250 cm$^{-1}$ | JOYSpectra $\gamma_1$ 3000 cm$^{-1}$ | JOYSpectra $\gamma_4$ 4000 cm$^{-1}$ | Ref. S32 | Ref. S33 |
| $S_1 \rightarrow S_0$ | $^7F_0 \rightarrow ^5D_0$ | 3.91E5 ex | |
| | $^7F_0 \rightarrow ^5D_1$ | 2.38E6 ex | 7.82E7 ex | 1.95E8 ex |
| | $^7F_0 \rightarrow ^5D_4$ | 1.60E5 mp | |
| | $^7F_0 \rightarrow ^5G_6$ | 1.33E4 mp | |
| | $^7F_0 \rightarrow ^5L_6$ | 3.18E4 mp | |
| $^7F_1 \rightarrow ^5D_0$ | | 2.28E6 ex | 1.54E7 ex |
Table S6. Comparison of our results for ET rates of Eu(TTA)$_3$(H$_2$O)$_2$ using the software LUMPAC and JOYSpectra with those from Refs. 32,33, as described above. (The mechanisms are given as ex – exchange; dd – dipole-dipole; dm – dipole-multipole; mp - multipolar). We consider that ET only occurs from the lowest singlet state, not higher ones. Note that the T$_1$ → T$_0$, 7F$_0$ → 5D$_1$ rate is 23 times higher than in Table 3 of the manuscript.

C. Calculations employing the model of Malta but with some parameters taken from the present study.

The aim of the following is to show that simple calculations can be made without recourse to software since many matrix elements are zero.

This Section gives our calculations of ET rates for examples of some transitions in Eu(TTA)$_3$(H$_2$O)$_2$ using the model of Malta, with the spectral overlap integral and dipole strength (calculated from oscillator strength) taken from the present study. In conclusion, the ED-ED transfer rates are calculated in the region of 10$^5$ s$^{-1}$ but the ED-EQ rate for S$_1$ → S$_0$, 7F$_0$ → 5D$_2$ is within an order of magnitude of that calculated in Table 2 of the manuscript for ED-ED transfer.

Reduced spin matrix elements. The squared reduced spin matrix elements of Eu$^{3+}$ have been taken by Malta’s group from the free ion wavefunctions of Ofelt.$^{33}$ The ground state 7F$_0$ has four SLJ components and other free ion terms have up to ten. Professor Y. Y. Yeung kindly provided to us the free ion compositions, comprising 10 SLJ components for each multiplet term, calculated with 6 decimal places from the fits of the energy levels of Cs$_2$NaEuCl$_6$, LaF$_3$:Eu$^{3+}$ and NaCdPO$_4$:Eu$^{3+}$ so that we could check if the reduced matrix elements show any dependence upon Eu$^{3+}$ coordination. We employed the formula for the matrix element:
\[ <ψLS||S||ψ'LS'J'> = \sum_i a_i <ψLS||S||ψ'LS'J'>_i \quad \text{(S5)} \]

Where \(a_i\) represents the product of the compositions of initial and final states, and

\[ <ψLS||S||ψ'LS'J'>_i = \delta_{\psi_L\psi_L'}\delta_{\psi_S\psi_S'}(-1)^{L+S+j+1}[(2J+1)(2J'+1)S(S+1)(2S+1)]^{1/2} \begin{pmatrix} S & J & L \\ J' & S' & 1 \end{pmatrix} \quad \text{(S6)} \]

Note the power of (-1). Our results in the Table S7 show generally similar squared matrix elements for the three systems, with oxygen coordination having the lower values, although there are some differences with the tabulation of Ref. 35. The value of the matrix element depends upon the number of intermediate coupled states chosen. For \(|<\psi F_o||S||3D_2>|^2\), the \(6j\) symbol gives the value zero for our included states, but a value of 0.0009 has been reported.\(^\text{36}\)

Table S7. Calculated squared reduced spin matrix elements, \(|<ψLS||S||ψ'LS'J'>|^2\).

| Squared matrix element | This work | Ref. S35 (From Ref. S34) |
|------------------------|-----------|-------------------------|
| \(|<\psi F_0||S||3D_1>|^2\) | 0.02081 | 0.02097 0.02058 0.0273 |
| \(|<\psi F_0||S||3D_2>|^2\) | 0 0 0 - |
| \(|<\psi F_1||S||3D_1>|^2\) | 0 0 0 - |
| \(|<\psi F_1||S||3D_2>|^2\) | 0.11090 0.11182 0.1089 0.117 |
| \(|<\psi F_1||S||3D_3>|^2\) | 1.64882E-7 1.64882E-7 1.15213E-7 2.81E-5 |
| \(|<\psi F_2||S||3D_3>|^2\) | 9.61608E-3 9.62634E-3 9.48934E-3 4.58E-3 |

**Electric dipole-electric dipole energy transfer in Eu(TTA)₃(H₂O)₂**. The equation given in Ref. S20 for ED-ED ET, with the symbols defined therein, is:

\[ W_{\text{d-d}} = \frac{S_L(1-\sigma_i)^2}{2J+1} \frac{4\pi e^2}{\hbar} \sum_{\lambda} \Omega_{\lambda}^{\text{FED}} <ψ'J'||U(\lambda)||ψJ'>^2 F \quad \text{(S7)} \]

where: \(W\) (s⁻¹) = \((S_L\) (esu² cm²) \(e^2\) (esu²) \(F\) (erg⁻¹) \(\Omega\) (cm²))/\(h\) (erg s) \(R^6\) (cm⁶))

and we use the values of the dipole strength \(S_L\) and \(F\) from the present study.

Consider \(S_1 \rightarrow S_0\) and \(7F_0 \rightarrow 5L_6\):

\[ e = 4.8032\times10^{-10} \text{ cm}^{3/2}\text{g}^{1/2}\text{s}^{-1}; \quad h/2\pi = 1.0546\times10^{-27} \text{ cm}^2\text{g}^{-1}\text{s}^{-1}; \quad R_L = 4.5\times10^{-8} \text{ cm}; \quad F = 0.172 \text{ eV}^{-1} = 1.0735\times10^{11} \text{ erg}^{-1}. \]

Take the singlet oscillator strength maximum value 0.05 (c.f. Eq. 7):

\[ S_L = \frac{3he^2}{8\pi^2\nu V G_i(n^2+2)^2} P_{J} \sim 1.53\times10^{-35} \text{ esu}^2 \text{ cm}^2 \quad \text{(S8)} \]

The \(U^{(\lambda)}\) matrix elements are zero for \(\lambda = 2\) and for \(\lambda = 6\) it is 0.0153, for \(|<\psi L_6||U^{(6)}||7F_0>|^2\).

\(\Omega_{\lambda}^{\text{FED}}\) from JOYSpectra are \(\lambda = 2, 8.068\text{E-22}; \lambda = 4, 8.246\text{E-22}; \lambda = 6, 1.662\text{E-21} \text{ cm}^2\). We only need \(\lambda = 6\).
\( J = 0 \) for the acceptor level \( ^7F_0 \) and \( G = 1 \) for the donor \( S_1 \). \( \sigma_1 = 0.66917. \) So, putting in these numbers, and correcting for the ground state population (say, by the factor of 0.6), \( W_{ET} \sim 9.08 \times 10^5 \text{s}^{-1} \). The mixing with \( ^7F_2 \) and contribution from \( ^7F_1 \) have not been considered.

**Consider \( S_1 \rightarrow S_0 \) and \( ^7F_0 \rightarrow ^5D_2 \):**

The \( U^{(k)} \) matrix elements are given as zero in JOYSpectra so that the respective ET rates are zero. However, the \( U^{(2)} \) matrix element squared has been reported as 0.0009 for oxide systems.\(^{336}\) Noting that \( \Omega_2^{ET} \approx 8.068 \times 10^{-22} \), and from Table 1, \( F = 1.335 \times 6.241496 \times 10^{11} \text{erg}^{-1} \), and correcting for the ground state population, \( W_{ET} \sim 2.01 \times 10^5 \text{s}^{-1} \).

**Consider \( S_1 \rightarrow S_0 \) and \( ^7F_0 \rightarrow ^5D_{0,1} \):**

The squared matrix element \( | | < \psi J' \| U^{(k)} \| \psi J > |^2 \) is zero for these cases, in the absence of \( J \)-state mixing so that the values are zero.

**Electric dipole-electric multipole energy transfer in \( \text{Eu(TTA)}_3(\text{H}_2\text{O})_2 \).** The equation in Ref. S20, with definitions therein, in cgs units, is:

\[
W_{d-m} = \frac{S}{(2J+1)C} \frac{2\pi e^2}{\hbar} \sum \lambda (\lambda + 1) \frac{<r^2>^2}{(\hat{R}^2)^2} < f || C^{(\lambda)} || f >^2 (1 - \sigma_\lambda)^2 < \psi J' \| U^{(\lambda)} \| \psi J >^2 F
\]

where \( \lambda = 2,4,6 \); the radial integrals: \( <r^2> = 0.916 \text{a.u.}; <r^4> = 2.017 \text{a.u.}; <r^6> = 9.025 \text{a.u.}; <r^8> = 82.089 \text{a.u.} \), and 1 Bohr = 5.2917712067121 \( \times 10^{-8} \) cm. The Racah operator integrals: \( <3 || C^2 || 3 > = -1.366; <3 || C^4 || 3 > = 1.128; <3 || C^6 || 3 > = -1.27 \). The values of \( \sigma_\lambda \) are uncertain and are taken from Ref. S32 as \( \sigma_2 = 0.6; \sigma_4 = 0.139; \sigma_6 = 0.1 \). The corresponding values in JOYSpectra are 0.512, 0.019 and -0.0308, respectively.

Taking the acceptor level \( J = 0 \), the donor state \( G = 1 \), in addition to \( R_c = 4.5 \text{Å} \), and the value of \( S_1 \) as above \((1.53 \times 10^{-35} \text{esu}^2 \text{cm}^4)\), we have, considering singlet ET:

For \( \lambda = 2 \):

\[
W_{d-m} = \frac{S}{(2J+1)C} \frac{2\pi e^2}{\hbar} \sum \lambda (\lambda + 1) \frac{<r^2>^2}{(\hat{R}^2)^2} < 3 || C^{(2)} || 3 >^2 (1 - \sigma_2)^2 < \psi J' \| U^{(2)} \| \psi J >^2 F
\]

\[W_{d-m} = 0.737026 < \psi J' \| U^{(2)} \| \psi J >^2 F\] (S10a)

For \( \lambda = 4 \):

\[
W_{d-m} = \frac{S}{(2J+1)C} \frac{2\pi e^2}{\hbar} \sum \lambda (\lambda + 1) \frac{<r^2>^2}{(\hat{R}^2)^2} < 3 || C^{(4)} || 3 >^2 (1 - \sigma_4)^2 < \psi J' \| U^{(4)} \| \psi J >^2 F
\]

\[W_{d-m} = 3.598 \times 10^{-3} < \psi J' \| U^{(4)} \| \psi J >^2 F\] (S11a)

For \( \lambda = 6 \):

\[
W_{d-m} = \frac{S}{(2J+1)C} \frac{2\pi e^2}{\hbar} \sum \lambda (\lambda + 1) \frac{<r^2>^2}{(\hat{R}^2)^2} < 3 || C^{(6)} || 3 >^2 (1 - \sigma_6)^2 < \psi J' \| U^{(6)} \| \psi J >^2 F
\]

\[W_{d-m} = 2.671 \times 10^{-5} < \psi J' \| U^{(6)} \| \psi J >^2 F\] (S12a)
so that the ratios of \( W_{d-m} \) are 1:4.9x10^{-3}:3.6x10^{-5} for \( \lambda = 2,4,6 \), assuming equal squared reduced matrix elements and overlap integrals in Eqs. S10b, S11b and S12b. Alternatively, taking the values above of \( \sigma_i (i = 2,4,6) \) as in JOYSpectra, the numerical values in Eqs. S10b-S12b are 1.09699, 4.67134x10^{-3} and 3.50435x10^{-5}, respectively, with the ratio of 1:4.3x10^{-3}:3.2x10^{-5}, so that there is not a great deal of difference. In the following, we employ the values of \( \sigma_i \) from Ref. S32.

Consider \( S_1 \rightarrow S_0 \) and \( ^7F_0 \rightarrow ^5L_6 \):

In Table S6, the largest values of \( W_{d-m} \) for the \( ^7F_0 \) acceptor set are for \( ^5\text{L}_6, ^5\text{D}_4 \) and \( ^5\text{G}_6 \). We do not consider the latter two because their energies lie above \( S_1 \rightarrow S_0 \). For \( ^5\text{L}_6 \), the squared \( U^{(3)} \) matrix elements are zero for \( \lambda = 2,4 \) and for \( \lambda = 6 \) the value is 0.0153. The value of the spectral overlap integral in Table 1 is 1.0735x10^{11} \text{ erg}^{-1}, so that the calculated multipolar ET rate after correcting for the population of \( ^7F_0 \), is 2.63x10^4 \text{ s}^{-1}, without back-transfer.

Consider \( S_1 \rightarrow S_0 \) and \( ^7F_0 \rightarrow ^5D_2 \):

For \( ^7F_0 \rightarrow ^5D_2, [U^{(2)}]^2 \) = 0.0009, \( F = 8.332397 \times 10^{11} \text{ erg}^{-1} \), so that from S10(b), correcting for \( ^7F_0 \) population, \( W_{ET} \approx 3.32 \times 10^8 \text{ s}^{-1} \).

Energy transfer in \( \text{Eu(TTA)}_3(\text{H}_2\text{O})_2 \) by the exchange mechanism. The formula given in Ref. S20, with definitions, for the exchange mechanism is:

\[
W_{ex} = \sum (1-\sigma_0)^2 \frac{8\pi e^2}{(2J+1)G^3 \hbar^2 R_L^4} < |\Psi_j||S||\Psi_j|^2 \sum_m | < \Psi^{-1}_N\Pi||\sum_j r_j C_0^{(1)}(j) S_{-m}(j) | \Psi^{-1}_N\Pi^* |)^2 \quad (S13a)
\]

and it has been approximated as:\textsuperscript{520}

\[
W_{ex} \approx \frac{(1-\sigma_0)^2 8\pi e^2}{(2J+1)G^3 \hbar^2 R_L^4} S_j' F \quad (S13b)
\]

Where \( S_j' \) is the dipole strength of the ligand transition. The value of \( \sigma_0 \) in JOYSpectra is 0.99288. Taking \( R_L = 4.5 \text{ Å}, J = 0 \) and \( G = 3 \) for triplet ET, we have:

\[
W_{ex} = 1.8881 \times 10^{33} \quad \frac{< \Psi_j' ||S|| \Psi_j'^2 > S_j' F}{2} \quad (S14)
\]

In Malta’s original paper,\textsuperscript{537} in a slightly modified equation, the squared matrix element was taken as 0.04, the dipole strength 10^{-36} \text{ esu}^2 \text{ cm}^{-2}, \( R_L = 4 \text{ Å}, \sigma_0 = 0 \). Furthermore, the values \( \gamma_L = 5000 \text{ cm}^{-1} \) and \( \Delta = 1000 \text{ cm}^{-1} \) lead to \( F = 4.6x10^{11} \text{ erg}^{-1} \). Using his Eq. 11 and 12 in Ref. S37, we calculate \( W_{ET} = 1.3x10^{13} \text{ s}^{-1} \), and \( S_j' = 7.8x10^{12} \text{ s}^{-1} \) allowing for the population of \( ^7F_0 \), compared to his statement that the ET is of the order \( 10^{12} \text{ s}^{-1} \). This value is too high.

Consider \( T_1 \rightarrow S_0 \) and \( ^7F_0 \rightarrow ^5D_1 \) exchange ET

Taking the triplet oscillator strength as in Table 2 (\( S_\ell \approx 2.0x10^{42} \text{ esu}^2 \text{ cm}^{-2} \)), \( F = 2.29 \text{ eV}^{-1} \approx 1.429x10^{12} \text{ erg}^{-1} \), \( |<^5\text{D}_1||S||^7\text{F}_0>|^2 = 2.73x10^2 \),\textsuperscript{535} we obtain \( W_{ET} = 147 \text{ s}^{-1} \). It is strange to obtain such a small answer, compared to the above and to Table S6 (\( \approx 10^6 \text{ s}^{-1} \)). Clearly, the value of \( S_\ell' \) in this case is much larger than just taking the value \( S_\ell \) from the triplet oscillator strength.
In JOYSpectra, the value of $S_1^-$ has been taken as $10^{-36}$ esu$^2$ cm$^2$. This would give the ET rate $7.4 \times 10^7$ s$^{-1}$ in Eq. S14, using $F = 1.429 \times 10^{12}$ erg$^{-1}$, $|<S_1^-||S||^7F_0>|^2 = 2.73\times10^2$. This ET rate is similar to the experimental value derived in the main text for the ET transition $T_1 \rightarrow S_0$ and $^7F_0 \rightarrow ^5D_1$ ($2.84 \times 10^7$ s$^{-1}$).

In conclusion, some of the approximations made in calculations employing the model of Malta have been highlighted, particularly with respect to the overlap integral $F$, the magnitude of the exchange integral, and the use of incorrect transition energies. It has also been demonstrated that such calculations can easily be performed by hand. For a discussion of the use of forced electric dipole (static coupling) and dynamic coupling matrix elements, and their cross-terms, for Eu$^{3+}$ complexes, the reader is referred to Refs. S14 and S16.

S9. Units and conversions used in this work

$a_0 = 5.291772... \times 10^{-11}$ m, Bohr radius

$\alpha = 7.297 \ 352 \ 5693 \ \times \ 10^{-3}$, Fine structure constant

$k_B = 0.6950356 \ \text{cm}^{-1} \ \text{K}^{-1}$, Boltzmann constant

$h = 6.62607004 \times \ 10^{-34}$ J s, Planck constant (kg m$^2$ s$^{-1}$)

$h = 1.0545718 \times \ 10^{-34}$ J s, 6.58211956x10$^{-16}$ eV s

$m = 9.10938356 \times 10^{-31}$ kg, electron mass

$e = 1.6021766208 \times 10^{-19}$ C, electron charge (A s)

$c = 2.99792458 \times 10^8$ m s$^{-1}$, the speed of light

$\varepsilon_0 = 8.854187817 \times 10^{-12}$ F m$^{-1}$, the vacuum permittivity (kg$^{-1}$ m$^3$ s$^4$ A$^2$)

$P_x$ oscillator strength of X, dimensionless

1 eV = 1239.84193 nm; 1 eV = 1.60218x10$^{-19}$ J; 1 eV = 8065.54429 cm$^{-1}$

1 eV$^{-1}$ = 6.2415x10$^{11}$ erg$^{-1}$; 1 eV = 1.60218x10$^{-12}$ erg

1 cm$^3$ = 1.98644587x10$^{-23}$ J = 1.239841984x10$^{-4}$ eV

1 s$^{-1}$ = 4.13558x10$^{-15}$ eV

1 J = 10$^7$ erg, 1 J$^{-1}$ = 10$^{-7}$ erg$^{-1}$

$L = 6.02214076x10^{23}$ mol$^{-1}$

ESU unit statcoulomb, 1 statC = 3.335641x10$^{-10}$ C and 1 cm$^2$ = 10$^{-2}$ m, so that $1 \text{ esu}^2 \text{ cm}^2 = (3.335641 \times 10^{-10} \text{ C})^2 \times (10^{-2} \text{ m})^2 = 1.112650 \times 10^{-23} \text{ C}^2 \text{ m}^2$, or $1 \text{ C}^2 \text{ m}^2 = 8.987552 \times 10^{22} \text{ esu}^2 \text{ cm}^2$.
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