Intrinsic quantum yields and radiative lifetimes of lanthanide tris(dipicolinates)

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Table S1. Doubly reduced matrix elements used in the calculations of the dipole strengths for absorption and emission of $Cs_3[Eu(dpa)_3]$.[42-44]

Transition	Element	Value	Transition	Element	Value
$^5D_2 \leftarrow {}^7F_0$	$\left\vert\langle\Psi\Vert U^2\Vert\Psi'\rangle\right\vert$	0.0008	$^5D_0 \rightarrow {}^7F_2$	$\left\vert\langle\Psi\Vert U^2\Vert\Psi'\rangle\right\vert$	0.0032
$^5L_6 \leftarrow {}^7F_1$	$\left\vert\langle\Psi\Vert U^6\Vert\Psi'\rangle\right\vert$	0.0090	$^5D_0 \rightarrow {}^7F_4$	$\left\vert\langle\Psi\Vert U^4\Vert\Psi'\rangle\right\vert$	0.0023
$^5L_6 \leftarrow {}^7F_0$	$\left\vert\langle\Psi\Vert U^6\Vert\Psi'\rangle\right\vert$	0.0155	$^5D_0 \rightarrow {}^7F_6$	$\left\vert\langle\Psi\Vert U^6\Vert\Psi'\rangle\right\vert$	0.0002
$^5D_4 \leftarrow {}^7F_0$	$\left\vert\langle\Psi\Vert U^4\Vert\Psi'\rangle\right\vert$	0.0011			

Table S2. Doubly reduced matrix elements used in the calculations of the dipole strengths for absorption[44] and emission[40] of $Cs_3[Tb(dpa)_3]$.

Transition	$\left\vert\langle\Psi\Vert U^2\Vert\Psi'\rangle\right\vert^2$	$\left\vert\langle\Psi\Vert U^4\Vert\Psi'\rangle\right\vert^2$	$\left\vert\langle\Psi\Vert U^6\Vert\Psi'\rangle\right\vert$	$\left\vert\langle\Psi\Vert L+2S\Vert\Psi'\rangle\right\vert$
$^5D_4 \leftarrow {}^7F_6$	0.0010	0.0008	0.0013	
$^5D_3 \leftarrow {}^7F_6$ $^5G_6 \leftarrow {}^7F_6$	} 0.0017	0.0047	0.0132	
$^5L_{10} \leftarrow {}^7F_6$	0.00000	0.00040	0.05920	
$^5D_4 \rightarrow {}^7F_0$	0.00066	0.00156	0.00187	
$^5D_4 \rightarrow {}^7F_1$	0.01459	0.00109	0.00356	
$^5D_4 \rightarrow {}^7F_2$	0.00034	0.00187	0.00193	
$^5D_4 \rightarrow {}^7F_3$	0.00269	0.00047	0.00074	0.128
$^5D_4 \rightarrow {}^7F_4$	0.00090	0.00040	0.00013	0.004
$^5D_4 \rightarrow {}^7F_5$	0.00000	0.00154	0.00000	0.728
$^5D_4 \rightarrow {}^7F_6$	0.00000	0.00246	0.00000	

Table S3. Quantum yield and related data (see main text for definitions) of $Cs_3[Ln(dpa)_3]$, Ln = Eu, Tb versus concentration in Tris-HCl 0.1 M.

c / M	$(L_a\text{-}L_c)$ /10^{-7}	α	E_c / 10^6	$(Q \pm 2\sigma)$ /%	% (tris species)
Ln = Eu					
4.56×10^{-4}	3.308	0.91	8.93	27.0 ± 0.1	92.9
2.28×10^{-4}	2.820	0.71	7.35	26.4 ± 0.7	90.0
1.14×10^{-4}	2.051	0.55	5.08	24.8 ± 0.5	86.2
5.70×10^{-5}	1.200	0.33	2.90	24.2 ± 0.6	81.1
2.85×10^{-5}	0.602	0.16	1.41	22.7 ± 1.4	74.4
1.43×10^{-5}	0.270	0.07	0.65	24.1 ± 1.0	65.9
Ln = Tb					
4.52×10^{-4}	3.325	0.89	7.54	22.6 ± 0.1	95.0
2.26×10^{-4}	2.642	0.55	5.95	22.5 ± 0.3	93.0
1.13×10^{-4}	1.774	0.30	4.01	22.4 ± 0.5	90.2
5.65×10^{-5}	1.034	0.15	2.28	22.1 ± 0.7	86.4
2.82×10^{-5}	0.618	0.08	1.33	21.4 ± 0.2	81.4
1.41×10^{-5}	0.270	0.03	0.646	24.0 ± 2.8	74.7

Table S4. Quantum yields of $Cs_3[Ln(dpa)_3]$, Ln = Eu (6.7×10^{-5} M), Tb (6.6×10^{-5} M), versus pH. Excitation wavelength: 280 nm.

Ln = Eu		Ln = Tb	
pH	($Q \pm 2\sigma$) / %	pH	($Q \pm 2\sigma$) / %
2.36	2.6 ± 0.2	2.65	10.0 ± 0.1
3.11	6.8 ± 0.2	3.23	16.2 ± 0.9
4.16	24.0 ± 1.4	4.36	20.0 ± 0.3
5.10	24.8 ± 1.7	4.94	20.7 ± 0.6
5.90	24.6 ± 0.5	5.81	20.1 ± 0.9
6.97	25.9 ± 1.1	7.06	21.0 ± 0.1
8.04	24.8 ± 1.3	8.42	21.0 ± 1.0
8.83	23.5 ± 1.8	9.12	21.0 ± 1.3
10.06	25.7 ± 0.9	10.02	21.2 ± 0.5

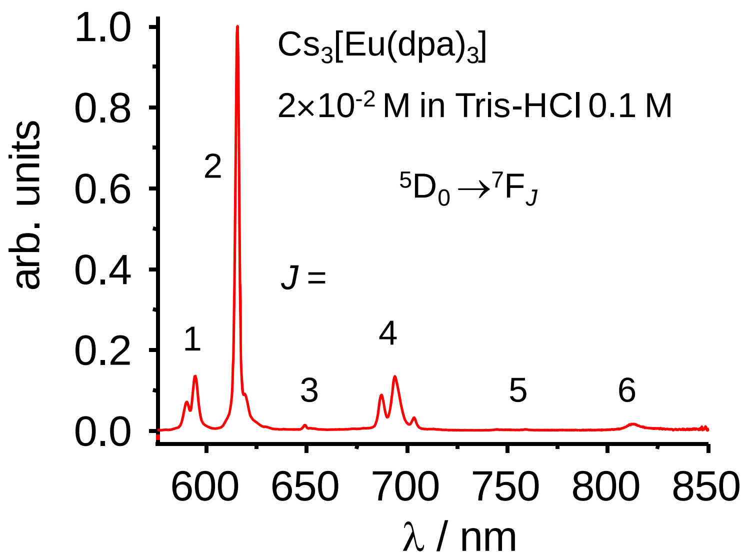

Figure S1. Emission spectrum of $Cs_3[Eu(dpa)_3]$ in Tris-HCl under ligand excitation (280 nm).

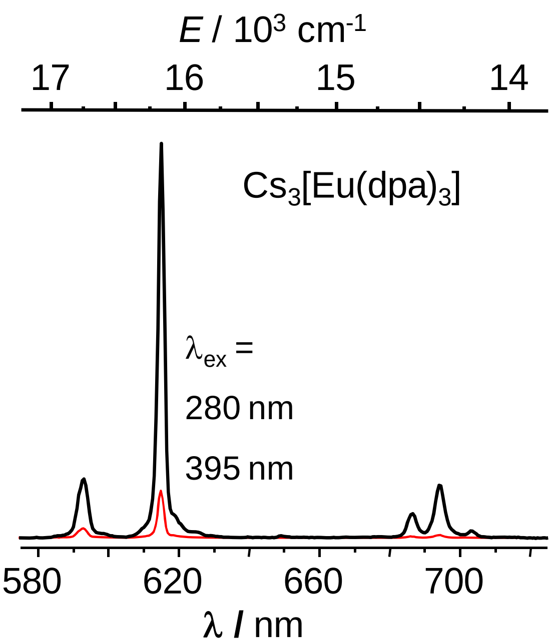

Figure S2. Emission spectra of a microcrystalline sample of $Cs_3[Eu(dpa)_3]$ under ligand excitation (280 nm) and direct f-f excitation (395 nm, $^5L_6 \leftarrow {}^7F_0$, dotted line).