

Electronic Supplementary Information (ESI)

**Energy Transfer in Coumarin-Sensitised Lanthanide Luminescence:
Investigation of the Nature of the Sensitiser and its Distance to the Lanthanide
Ion**

Julien Andres, Anne-Sophie Chauvin

École Polytechnique Fédérale de Lausanne, ISIC, BCH 1405, CH-1015 Lausanne, Switzerland

SUPPLEMENTARY MATERIAL

8 pages

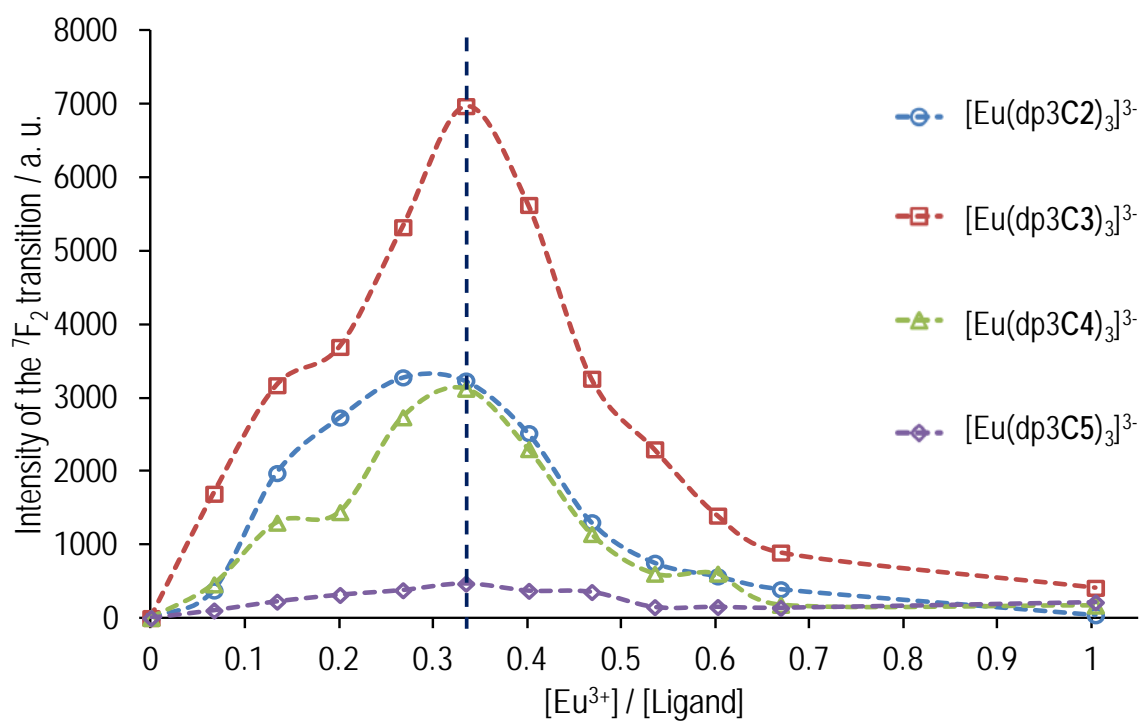


Figure S1. Intensity of the ${}^5D_0 \rightarrow {}^7F_2$ transition of europium(III) upon titration of $3 \cdot 10^{-4}$ M aqueous solutions (Tris-buffered, pH 7.4) of each dp3Cy ligand by europium perchlorate. Maximal emission reached at $\frac{1}{3}$ of europium per ligand ratio. The lifetime at those maxima is 1.4 ms for all the ligands.

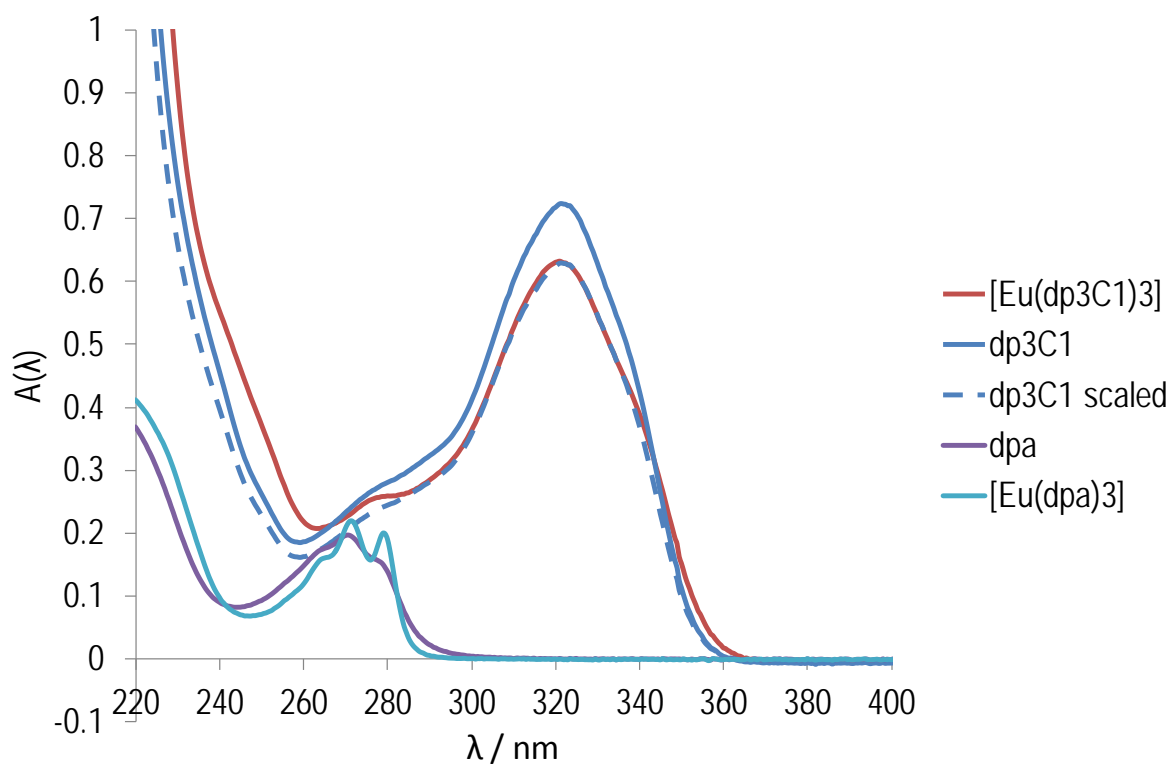


Figure S2. Absorption spectra of the free ligand dp3C1 and of the complex [Eu(dp3C1)₃] compared to the free ligand absorption scaled (dp3C1 scaled) to match the maximum absorbance above 300 nm and comparison with the effect of complexation between free dipicolinic acid (dpa) and its europium complex [Eu(dpa)₃]

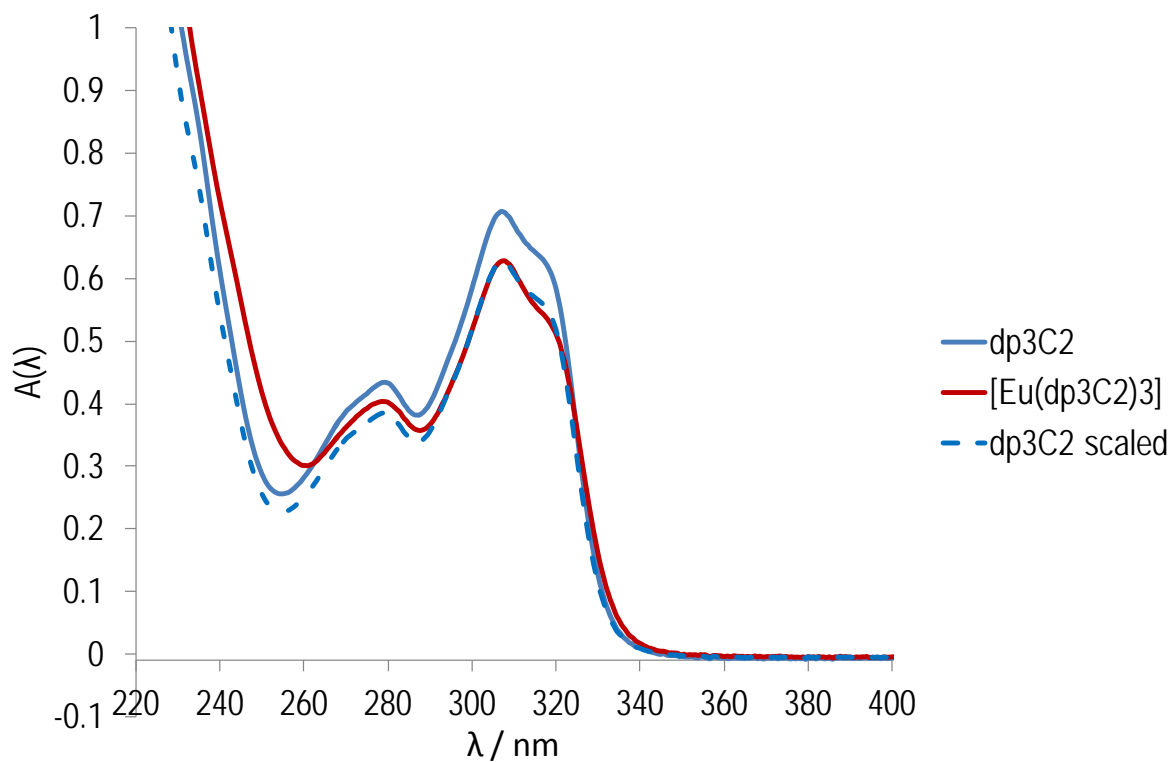


Figure S3. Absorption spectra of the free ligand dp3C2 and of the complex [Eu(dp3C2)₃] compared to the free ligand absorption scaled (dp3C2 scaled) to match the maximum absorbance above 300 nm

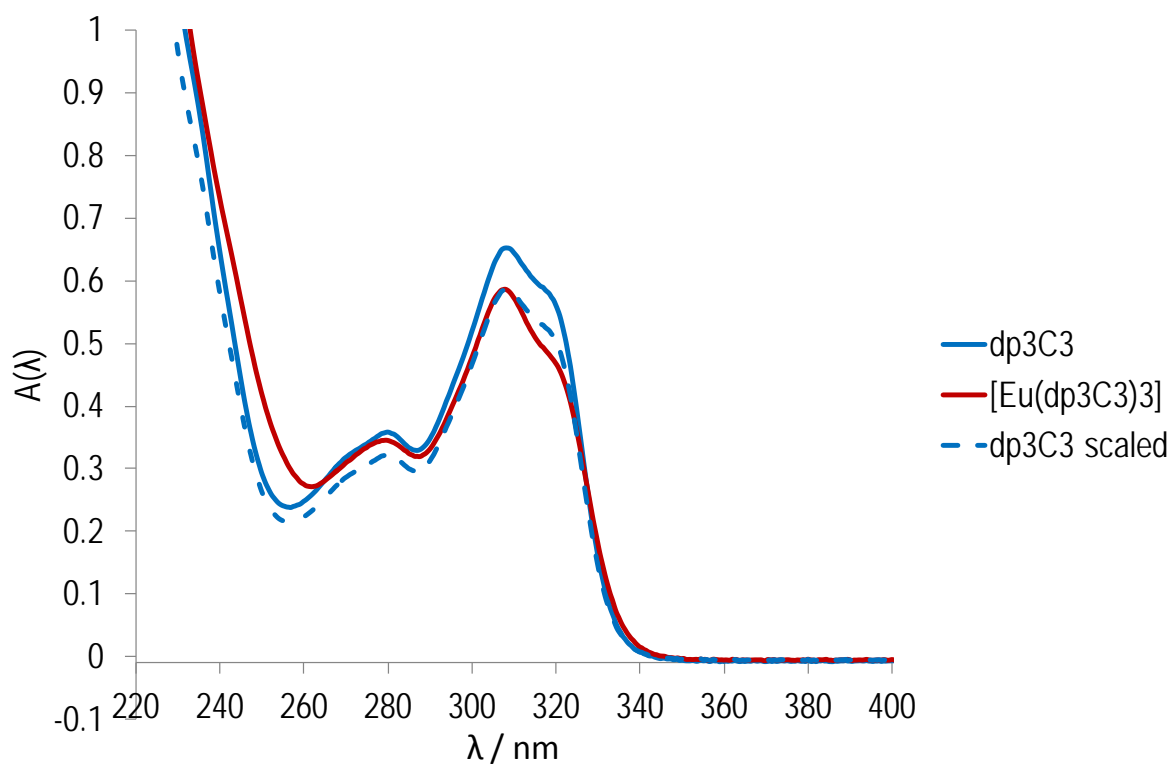


Figure S4. Absorption spectra of the free ligand dp3C3 and of the complex $[\text{Eu}(\text{dp3C3})_3]$ compared to the free ligand absorption scaled (dp3C3 scaled) to match the maximum absorbance above 300 nm

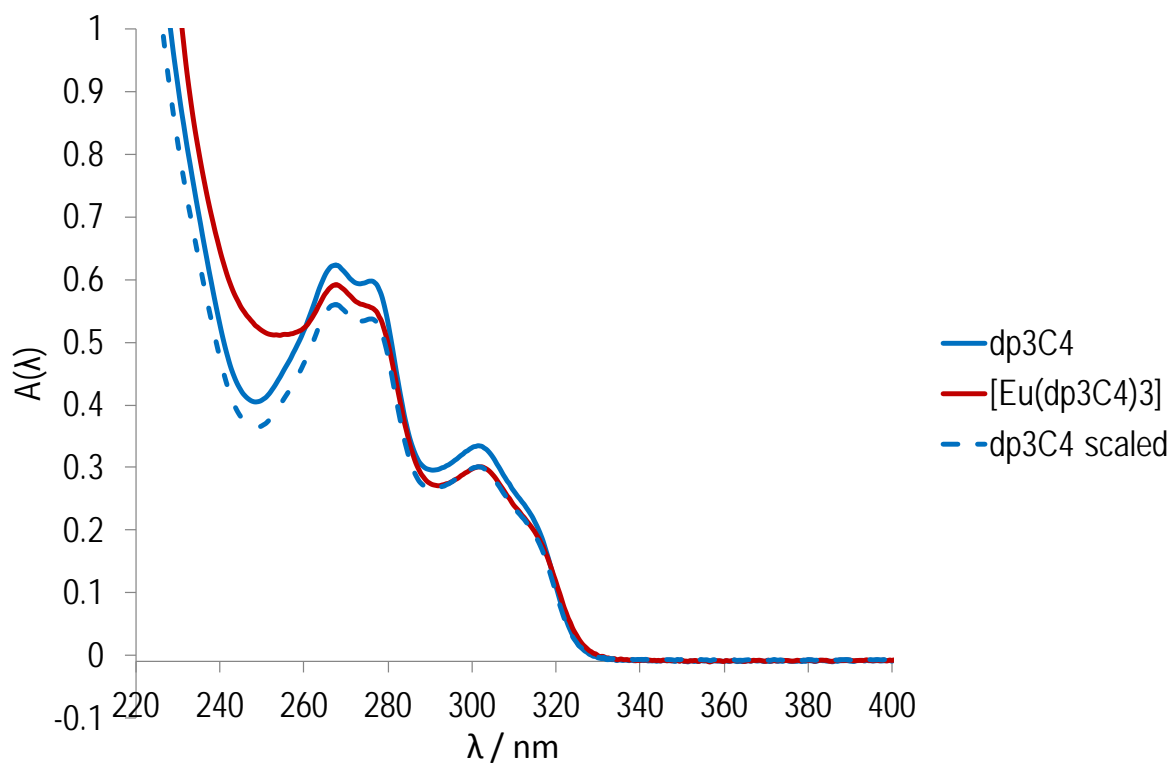


Figure S5. Absorption spectra of the free ligand dp3C4 and of the complex $[\text{Eu}(\text{dp3C4})_3]$ compared to the free ligand absorption scaled (dp3C4 scaled) to match the maximum absorbance above 300 nm

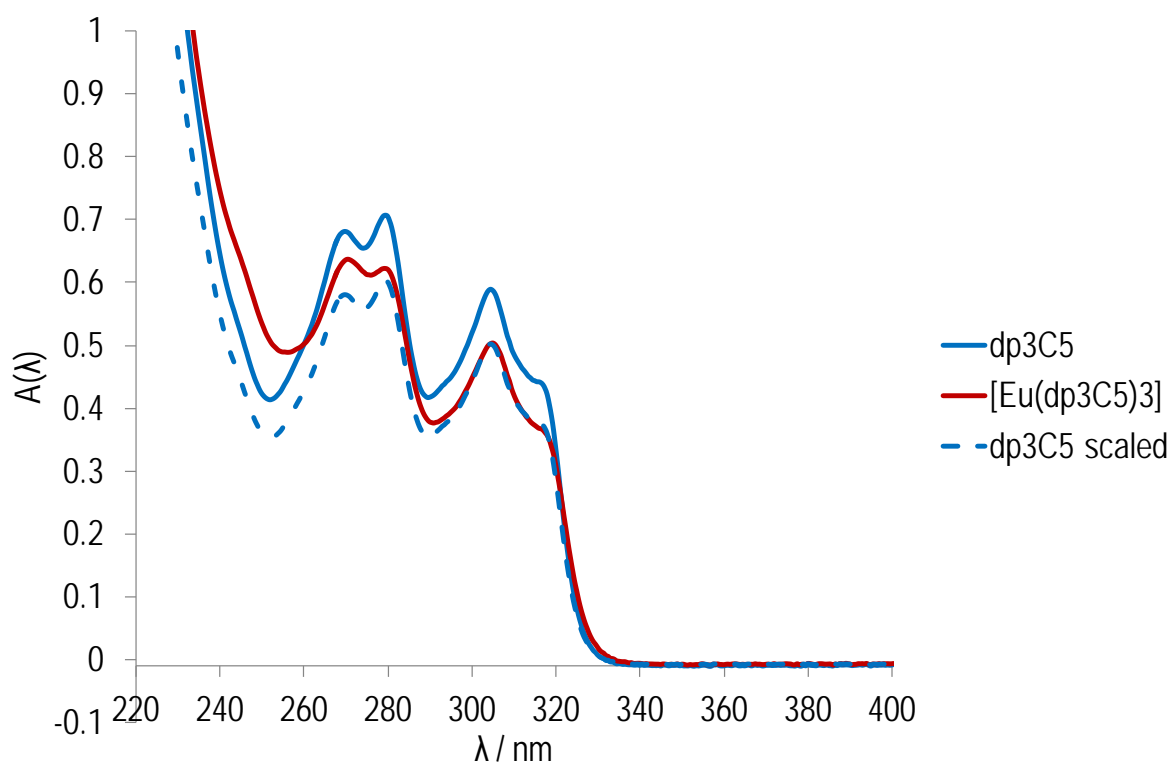


Figure S6. Absorption spectra of the free ligand dp3C5 and of the complex $[\text{Eu}(\text{dp3C5})_3]$ compared to the free ligand absorption scaled (dp3C5 scaled) to match the maximum absorbance above 300 nm

Table S1. Maxima of absorption (wavelength λ_{max} and extinction coefficient ϵ_{max}) of the $[\text{Eu}(\text{dp3Cy})_3]^{3-}$ complexes in Tris-buffered aqueous solution, pH 7.4. ^s shoulder

$[\text{Eu}(\text{dp3Cy})_3]^{3-}$	$\lambda_{\text{max}} / \text{nm}$	$\epsilon_{\text{max}} / \text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$
y = 1	279 ; 320 ; 339 ^s	12,950 ; 31,600 ; 20,400
y = 2	279 ; 307 ; 320 ^s	20,150 ; 31,350 ; 25,600
y = 3	279 ; 307 ; 320 ^s	17,300 ; 29,300 ; 23,450
y = 4	268 ; 276 ; 302 ; 315 ^s	29,600 ; 27,800 ; 15,100 ; 9,900
y = 5	270 ; 279 ; 305 ; 317 ^s	31,800 ; 31,100 ; 25,200 ; 18,250

Table S2. Photophysical properties of the $[\text{Tb}(\text{dp3Cy})_3]^{3-}$ complexes (0.1 mM, Tris-buffered aqueous solution pH 7.4) at room temperature ($\lambda_{ex} = 320$ nm). Error of 10 % on the quantum yields (sensitised quantum yields of the europium emission Φ_L^{Eu} , quantum yields of the ligand-centred emission Φ_L^L) and ± 0.1 ms on τ_{obs} . N.d. values were too low to be determined with our experimental setup.

$[\text{Tb}(\text{dp3Cy})_3]^{3-}$	$\Phi_L^{\text{Tb}} / \%$	$\Phi_L^L / \%$	τ_{obs} / ms
y = 1	0.5	7.6	0.6
y = 2	1.4	1.0	1.6
y = 3	1.7	1.3	1.6
y = 4	n.d.	n.d.	1.8
y = 5	0.3	n.d.	1.7

Table S3. Quantum yield of the free ligands (0.3 mM, Tris-buffered aqueous solution, pH 7.4)

dp3Cy ²⁻	$\Phi_L^L / \%$
y = 1	31.0
y = 2	1.6
y = 3	2.5
y = 4	n.d.
y = 5	n.d.

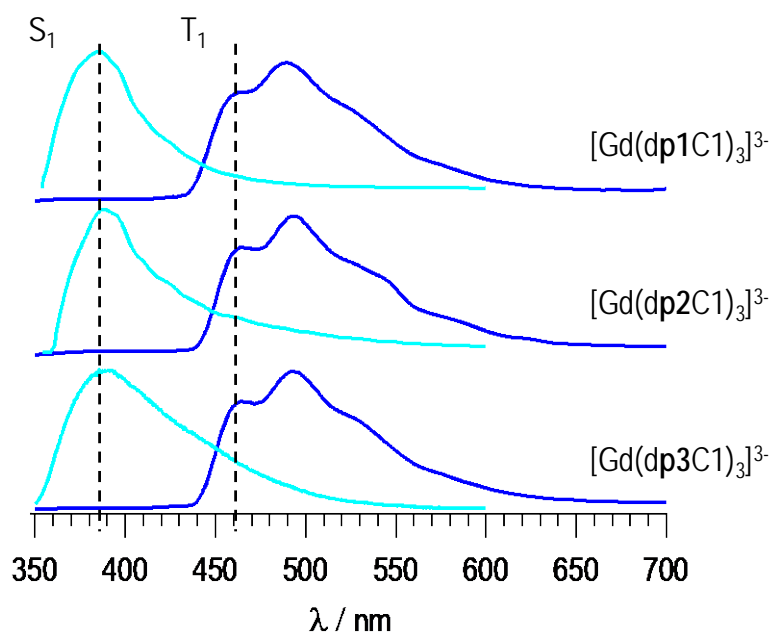


Figure S7. Fluorescence and phosphorescence spectra of the $[Gd(dpxC1)_3]^{3-}$ complexes at room temperature and at 77 K (50 μs after pulsed excitation) respectively. $\lambda_{\text{ex}}=320$ nm, 0.1 mM in Tris-buffered aqueous solution, pH 7.4. 10 % glycerol for the measurements at 77 K.

Derivation of the sensitisation efficiency from the rate of lanthanide population

$$\begin{aligned}
 \frac{d[Ln^*]}{dt} &= +k_{et}^S \cdot [S^*] + k_{et}^T \cdot [T^*] \\
 &= +k_{et}^S \cdot [S^*]_0 \cdot \exp(-k_{obs}^S \cdot t) + k_{et}^T \cdot [T^*]_0 \cdot \exp(-k_{obs}^T \cdot t) \\
 [T^*]_0 &= \eta_{isc} \cdot [S^*]_0 \\
 \eta_{isc} &= \frac{k_{isc}}{k_{obs}^S} \\
 \frac{d[Ln^*]}{dt} &= +[S^*]_0 \left[k_{et}^S \cdot \exp(-k_{obs}^S \cdot t) + k_{et}^T \cdot \eta_{isc} \cdot \exp(-k_{obs}^T \cdot t) \right] \\
 \Rightarrow [Ln^*] &= \int_0^{\tau} [S^*]_0 \cdot \left[k_{et}^S \cdot \exp(-k_{obs}^S \cdot t) + k_{et}^T \cdot \eta_{isc} \cdot \exp(-k_{obs}^T \cdot t) \right] \cdot dt \\
 &= [S^*]_0 \cdot \left\{ \left[\frac{k_{et}^S \cdot \exp(-k_{obs}^S \cdot \tau)}{-k_{obs}^S} + \frac{k_{et}^T \cdot \eta_{isc} \cdot \exp(-k_{obs}^T \cdot \tau)}{-k_{obs}^T} \right] - \left[\frac{k_{et}^S \cdot \exp(-k_{obs}^S \cdot 0)}{-k_{obs}^S} + \frac{k_{et}^T \cdot \eta_{isc} \cdot \exp(-k_{obs}^T \cdot 0)}{-k_{obs}^T} \right] \right\} \\
 &= [S^*]_0 \cdot \left\{ [0] - \left[\frac{k_{et}^S \cdot 1}{-k_{obs}^S} + \frac{k_{et}^T \cdot \eta_{isc} \cdot 1}{-k_{obs}^T} \right] \right\} = [S^*]_0 \cdot \left[+\frac{k_{et}^S}{k_{obs}^S} + \frac{k_{et}^T \cdot \eta_{isc}}{k_{obs}^T} \right] = [S^*]_0 \cdot (\eta_{et}^S + \eta_{et}^T \cdot \eta_{isc}) \\
 \Rightarrow \eta_{sens} &= \frac{[Ln^*]}{[S^*]_0} = \eta_{et}^S + \eta_{et}^T \cdot \eta_{isc}
 \end{aligned}$$