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ARTICLE TYPE

Efficient triazole-pyridine-bistetrazolate platform for highly luminescent lanthanide complexes

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I Experimental

General methods, equipment and chemicals used.

Solvents and starting materials were purchased from Sigma-Aldrich or Acros and used without further purification, unless otherwise stated. Lanthanide triflate salts were purchased from Aldrich and titrated for metal content before use, in the presence of EDTA and xylene orange.ⁱ ¹H and ¹³C NMR spectra were recorded at 298 K for characterization purposes on a Bruker Advance 200 and 400 MHz spectrometers. Chemical shifts are reported in ppm and were referenced internally to the residual solvent resonance. Mass spectra were run on a Thermo Scientific LXQ mass spectrometer equipped with an electrospray source. Elemental analyses were performed by the Centre régional de mesures physiques de l'Ouest (Rennes-1 University).

Luminescence measurements.

Absorption spectra were recorded in 1 cm quartz cells on a Cary 50 Probe UV-vis spectrophotometer. Low-resolution visible luminescence measurements in solution (spectra, lifetimes, triplet states, quantum yields) were recorded on a Perkin-Elmer LS-50B spectrometer at 298K. For spectra and triplet state measurements in solid state or methanol glass, the spectrometer was fitted with a solid state adaptor equipped with a liquid nitrogen cooling system. Quartz cells with an optical path of 1 cm were used for room temperature spectra, while 77K measurements were carried out in quartz capillaries 3 mm in diameter. The singlet state was measured in methanol solutions at room temperature, while the triplet state was determined in solid state at 77K after a 0.2 ms delay. In solid state, the measurements were also done on Fluorolog FL 3-22 spectrometer from Horiba-Jobin Yvon-Spex equipped with a double grating excitation monochromator and an iHR320 imaging spectrometer. Hamamatsu R928P and Hamamatsu R5509 photomultipliers were used for visible and NIR measurements, respectively. All spectra were corrected for detection and optical spectral response (instrumental functions) of the spectrofluorimeters. Quartz cells with an optical path of 1 cm and quartz capillaries 4 mm in diameter were used. Phosphorescence lifetimes were measured in time-resolved mode and are the averages of three independent measurements that were taken by monitoring the decay at the maxima of the emission spectra. The signals were analyzed with the OriginLab Origin Pro software.ⁱⁱ

The quantum yields were determined at room temperature through an absolute method using an integrating sphere from GMP S.A. (Switzerland) coupled to the spectrofluorimeter. The values reported are the average of three independent determinations for each sample. The absolute quantum yields were calculated using the following expressions:

$$\Phi = \frac{E_c}{L_a - L_c} = \frac{E_c}{L_a \cdot \alpha} \alpha = \frac{L_a - L_c}{L_a}$$

where *Ec*, *Lc* and *La* are the emission spectra of the sample, the excitation wavelength of the sample and the excitation wavelength of the reference, respectively.

Spectrophotometric titrations.

UV titrations were performed using a Cary 50 Probe UV/Vis spectrophotometer using a at 20°C (210-350 nm, 60 nm mn⁻¹ scan speed, spectral width 2 nm) using 1-cm Suprasil[®] quartz cells. Titrations of 10-mL samples were performed in a thermostated (20.0 \pm 0.1°C) glass-jacketed vessel filled with Ar, at $\mu = 1$ M (KCl); the pH values of the titrated solutions were controlled continuously. For the determination of conditional stability, titration of the ligand with Eu(OTf)₃ in methanol is used.

Deprotonation constants: A 2.5*10⁻⁵ M solution of ligand L1 in KCl 1 M was used.

Stability constants determination: A methanol solutions of L1 or L2 ($2.5*10^{-5}$ M) deprotonated with Et₃N and tetramethylammonium chloride (0.1 M) was titrated with a methanol solution of Eu(OTf)₃ ($6*10^{-4}$ M).

The data were computed and factor analysisⁱⁱⁱ and mathematical treatment of the spectrophotometric data were performed with the SPECFIT program.^{iv} Differences between the measured and the computed absorbances were less than 7×10^{-3} absorbance unit at any wavelength and exhibited statistical behaviour.

II. Ligands Synthesis and characterization



Scheme S1. (a) SOCl₂/DMF, EtOH (b) NaI/MeCN, CH₃COCl (c) NH₄OH/MeOH (d) TFAA/pyridine (e) Pd(Cl)₂(PPh₂)₃/CuI/TMS== (f) NaN₃/ NH₄Cl/DMF (g, h) n-octylN₃/K₂CO₃/CuSO₄/t-BuOH/H₂O

1. 120 ml of SOCl₂ were added to 12 g of chelidamic acid monohydrated (0.065 mol) in a 250 ml under argon and the heterogeneous mixture was cooled down at 0°C with an ice/water bath. 4 ml of anhydrous DMF were added and the resulting reaction mixture was refluxed overnight at 80 °C under argon atmosphere. Subsequently the thionyl chloride was removed by evaporation. To the resulting orange solid 150 ml of anhydrous EtOH were added and the system was stirred at 55 °C for 2 h and then at r.t. overnight. The crude mixture was evaporated, the residue was dissolved in dichloromethane and the resulting solution was washed with a NaHCO₃ saturated solution, water and brine; the solution was dried with anhydrous Na₂SO₄, filtrated and the solvent evaporated. Recrystallization of the residue from EtOH affords **1** as white needles (12.3 g, Yield = 73%). ¹H NMR (CDCl₃, 200MHz): 8.25 ppm (s, 2H), 4.48 ppm (q, J = 7.4 Hz, 4H), 1.44 ppm (t, J = 7.4 Hz, 6H).

2. NaI (71.55 g, 0.478 mol, 10 eq) was added to a solution of 12.3 g of **1** (0.048 mol, 1 eq) in 300 ml of acetonitrile, and the resulting mixture was stirred at r.t. for at least 2 h. Then, 10 ml of acetyl chloride (0.144 mol, 3 eq) were slowly added and the heterogeneous mixture was sonicated again for additional 2 h. 600 ml of dichloromethane and 150 ml of NaHCO₃ saturated solution were added. The organic phase was washed respectively with Na₂S₂O₃ saturated solution, water and brine; it was dried with Na₂SO₄ anhydrous, and then it was filtrated and evaporated to dryness. The yellowish solid was used without further purification (17 g, Yield = quantitative). ¹H NMR (CDCl₃, 200MHz): 8.61 ppm (s, 2H), 4.48 ppm (q, J = 7.4 Hz, 4H), 1.44 ppm (t, J = 7.4 Hz, 6H). ES-MS spectroscopy m/z: 372 [M+Na⁺], 350.1 [M+H⁺].

To a solution of 5 g of iodide (14.3 mmol, 1 eq) in 80 ml of MeOH 35 ml of ammonia solution 33% (20 eq) were added and the reaction was stirred at r.t overnight. After 18 h, the solution was dried and the desired product **2** was obtained as a white solid obtained (4.2 g, Yield = quantitative) and was used without further purification. ¹H NMR (CD₃SO, 200MHz): 8.87 ppm (bs, 1H), 8.48 ppm (s, 2H), 7.80 (bs, 1H).

3. To a solution of 4.2 g of **2** (0.0144 mol, 1 eq) in anhydrous dichloromethane (150 ml), 5.2 ml of anhydrous pyridine (0.063 mol, 4.4 eq) and 5 ml of trifluoroacetic anhydride (0.0345 mol, 2.4 eq) were added under argon. The reaction was stirred at r.t. for 24 h and then it was quenched by adding water (200 ml). The organic phase was washed with water until neutrality, it was dried with Na₂SO₄ anhydrous, filtrated and evaporated to dryness. The crude product was purified by flash chromatography (SiO₂, dichloromethane) to afford **3** as a white powder (2.5 g, Yield = 66%). ¹H NMR ((CD₃)₂SO, 200 MHz): 8.86 ppm (s). ES-MS spectroscopy m/z: not ionisable.

4. 1.6 g of **3** (6.27 mmol, 1 eq), 413 mg of $PdCl_2(PPh_3)_2$ (0.627 mmol, 0.1 eq), 224 mg of copper iodide (I) (1.25 mmol, 0.2 eq) were successively added under argon to a 1:1 solution of anhydrous tetrahydrofuran (60 ml) and triethylamine (60 ml). Finally, 3 ml of ethynyltrimethylsilane (21.9 mmol, 3.5 eq) were added and the reaction was left at 50 °C for 24 h in the dark. Then, the mixture was cooled, filtered over celite. The solution was evaporated and the solid dissolved in dichloromethane. The organic phase was washed with a saturated solution of ammonium chloride, water and brine, and then it was dried with Na₂SO₄ anhydrous, filtrated and evaporated to dryness. The black solid obtained was purified by flash chromatography (SiO₂, Et₂O/Petroleum Ether 9:1) to afford 1.1 g of **4 as** a light sensitive grey powder (Yield = 78.6%). ¹H NMR (CDCl₃, 200 MHz): 7.85 ppm (s, 2H), 0.28 (s, 9H). ¹³C NMR (CDCl₃, 50 MHz): 135.85 ppm, 135.54 ppm, 133.28 ppm, 115.50 ppm, 108.93 ppm, 98.19 ppm. ES-MS spectroscopy m/z: adding HCOOH, 226.1 [M+H⁺], 225.1 [M⁺].

H₂**L**₁. 100 mg of **4** (0.444 mmol, 1 eq), 178 mg of ammonium chloride anhydrous (3.33 mmol, 7.5 eq) and 216 mg of sodium azide (3.33 mmol, 7.5 eq) were successively added under argon to 20 ml of anhydrous DMF. The reaction was left at 125°C in the dark for 24 h. Then, the heterogeneous solution was cooled down, the salts were removed by filtration and the solvent evaporated. The residual solid was suspended in 30 ml of HCl 0.1M and stirred for at least 2h. The precipitated formed was filtered, washed with water and dried under vacuum to obtain H₂L₁ as a beige powder (125 mg, Yield = quantitative). ¹H NMR ((CD₃)₂SO, 200 MHz): 9.00 ppm (s, 1H), 8.76 ppm (s, 2H), 9-8 ppm (bbs, 3H). ES-MS spectroscopy m/z: 281.1 [M-H]⁻, 316.8 [M+Cl]⁻. **Elemental analysis** calcd. (%) for C₉H₆N₁₂ · 0.75 HCl · 0.35 **DMF**: C 36.02, H 2.77, N 51.61; found: C 36.19, H 2.61, N 51.43.

H₂**L**₂. 100 mg of **4** (0.44 mmol, 1 eq), 70 mg n-octylazide (0.44 mmol, 1eq), 14.2 mg of copper (II) sulphate (0.088 mmol, 0.2 eq), 35.2 mg of sodium ascorbate (0.177 mmol, 0.4 eq), 61.3 mg of potassium carbonate (0.44 mmol, 1eq) were successively added to a mixture of *t*-BuOH (5 ml) and water (5 ml). The reaction was left for 24 h at r.t. in the dark. Then, dichloromethane and ammonium hydroxide 5% were added to the reaction mixture and the organic phase was washed with water and brine, dried with anhydrous MgSO₄, filtered and evaporated to obtain a black oil. The crude product was purified by flash chromatography (Al₂O₃ activity III, dichloromethane/cyclohexane 7:3) to afford the triazole intermediate as a white solid (100 mg, Yield = 74%). ¹H NMR (CDCl₃, 200 MHz): 8.32 ppm (s, 2H), 8.11 ppm (s, 1H), 4.46 (t, J = 7.3 Hz, 2H), 1.97 (bt, J = 7 Hz, 2H), 1.36 (m, 8H), 0.87 (t, J = 10 Hz, 3H).

100 mg of triazole intermediate (0.32 mmol, 1 eq), 86.7 mg of anhydrous ammonium chloride (1.62 mmol, 5 eq), 105 mg of sodium azide (1.62 mmol, 5 eq) were successively added under argon to 20 ml of anhydrous DMF. The reaction was left at 125°C in the dark for 24 h. Then, the mixture was cooled down, the salts were filtered, the solvent was evaporated and the residual solid was suspended in 30 ml of HCl 0.1M. After at least 2 h of stirring, the resulting precipitated was filtered on a cellulose filter, washed with water and dried under vacuum to afford H_2L_2 as a white powder (73.4 mg, Yield = 57.3%). ¹H NMR ((CD₃)₂SO, 200 MHz): 9.44 ppm (s, 1H), 8.76 ppm (s, 2H), 4.47 ppm (t, 6.8 Hz, 2H), 1.90 ppm (bt, 2H), 1.25 ppm (m, 10 H), 0.84 ppm (t, J = 6.7 Hz, 3H). ES-MS spectroscopy m/z: 393.2 [M-H]⁻, 428.9 [M+Cl⁻]. **Elemental analysis** calcd. (%) for $C_{17}H_{22}N_{12} \cdot 0.15$ HCl \cdot 0.4 DMF: C 50.94, H 5.86, N 40.47; found: C 51.03, H 5.70, N 40.49.



A) ¹H NMR spectra (d6-DMSO, 200 MHz) of the H_2L_1 ligand (top) and of the deprotonated L_1^{2-} ligand (down); B) ¹H NMR spectra (d6-DMSO, 200 MHz) of the H_2L_2 ligand (top) and of the deprotonated L_2^{2-} ligand.

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III. Complexes synthesis and characterization

Figure S1. (A) L₁ ligand titration in 0.1 M TMACl MeOH (2.5*10⁻⁵ M) with Eu(OTf)₃. (B) L₂ ligand titration in 0.1 M TMACl MeOH (2.5*10⁻⁵ M) with Eu(OTf)₃.



Figure S2. UV-absorption spectra of the complexes [Eu(L_i)₃](NHEt₃)₃ (i=1,2), [Eu(pytzc)₃](NHEt₃)₃,), [Eu(pytz)₃](NHEt₃)₃ in methanol solutions and [Eu(dpa)₃]³⁻ in TRIS buffer (0.1 M) at 298K

Solutions of the homoleptic complexes $[Ln(L_i)_3](Et_3NH)_3$ (Ln = La, Pr, Eu, Tb for L = L1, Ln = Eu and Tb for L = L2) for spectroscopic characterizations were prepared in situ, by reacting three equivalents of ligand with one equivalent of lanthanide triflate in the presence of Et₃N.



Figure S3. ¹H NMR (CD₃OD, 400 MHz) of a 30 mM solution of [La(L₁)₃](Et₃NH)₃.



Figure S4. ¹H NMR (CD₃OD, 400 MHz) of a 26.5 mM solution of [Pr(L₁)₃](Et₃NH)₃.



Figure S5. ¹H NMR (CD₃OD, 400 MHz) of a 30 mM solution of [Tb(L₁)₃](Et₃NH)₃.

The isolated complexes have been prepared as follow

$[Eu(L_1)_3](Et_3NH)_3$

In a flask, 32.5 mg of H_2L_1 ligand (0.1 mmol, 1eq) were suspended in 1.5 ml MeOH, then 41.76 µl of Et₃N (0.3 mmol, 3 eq) were added, resulting in a clear yellow solution. A solution of 20.94 mg of Et(OTf)₃ (0.033 mmol, 0.33 eq) in 500 µl of MeOH was then added to the first solution. The mixture was stirred at r.t. for 2h. Slow diffusion of Et₂O into the resulting solution overnight affords the complex as thin yellow needles. The solid was collected, washed with Et₂O and dried under vacuum (28 mg, Yield = 95%,). ¹H NMR (CD₃OD, 200 MHz): 7.91 ppm (s, 1H), 5.54 ppm (s, 2H). ESI-MS spectroscopy m/z: 356.0 [Eu(L-2H)₂]², 713.1 [Eu(L-2H)₂]⁻.

$[Tb(L_1)_3](Et_3NH)_3$

This complex was prepared using the same procedure as for $[Eu(L_1)_3](Et_3NH)_3$ affording 25.2 mg of complex (Yield = 81.3%). ¹H NMR (CD₃OD, 200 MHz): 9.65 (bs, 2H), 7.95 (bbs, 1H). ESI-MS spectroscopy m/z: 359.0 [Tb(L-2H)₂-H]²⁻, 791.1 [Tb(L-2H)₂]⁻.



Figure S6. ¹H NMR (CD₃OD, 200 MHz) of [Eu(HL₁)₃](Et₃NH)₃ crystals.

[Eu(L₂)₃](Et₃NH)₃

Using the same procedure adopted for the L₁ ligand, we obtained 13.72 mg of white long needles (Yield = 62 %). ¹H NMR (CD₃OD, 200 MHz): 8.18 ppm (s, 1H), 5.55 ppm (s, 2H), 4.41 ppm (t, J = 7 Hz, 2H), 1.89 ppm (bt, 2H), 1.29 ppm (m, 10H), 0.89 ppm (bt, 3H). ESI-MS spectroscopy m/z: 937.3 [Eu(L-2H)₂]²⁻ (and some association).

[Tb(L₂)₃](Et₃NH)₃

With the same procedure as $[Eu(L_2)_3][Et_3NH]_3$, they were obtained 20.05 mg of white long needles (Yield = 95.4%). ¹H NMR (CD₃OD, 200 MHz): 9.91 ppm (bs, 2H), 8.05 ppm (bbs, 1H), 5.26 ppm (bt, 2H), 2.65 ppm (bt, 2H), 1.95-1.58 ppm (m, 10H), 1.09 (bs, 3H). ESI-MS spectroscopy m/z: 943.3 [Tb(L-2H)₂]⁻, 1336.8 [Tb(L-2H)₂+L]⁻.



Figure S7. ¹H NMR (CD ₃OD, 200 MHz) of [Eu(L₂)₃](Et₃NH)₃ crystals (top) and [Tb(L₂)₃](Et₃NH)₃ (down) with the relative assignment.



Figure S8. $[Eu(L_1)_3](Et_3NH)_3$ complex esi-mass spectrum (page before) and $[Eu(L_2)_3](Et_3NH)_3$ complex one (this page).

PVA doped film

Polyvinyl acetate (PVA) doped films of $[Ln(L_2)_3](Et_3NH)_3$ complex (Ln = Eu and Tb) were prepared by dissolving purified PVA pellets in dichloromethane (low molecular weight, 10% w/w) in the presence of the complex (2 mM). The films were obtained by drop-casting 200 µL of PVA doped solutions on borosilicate substrates (17.5 × 20 mm) leading to transparent film formation. Finally, the substrates were dried under vacuum for 2 h. Flexible doped films were obtained depositing PVA doped solutions (1 mL) by dropcasting on a Teflon substrate (25 × 25 mm) and dried under vacuum at room temperature for 2 days.

Polyvinyl acetate doped film of $[Tb(L_1)_3](Et_3NH)_3$ were prepared with the same procedure, but using methanol as solvent.

Solution Structure

In a paramagnetic lanthanide complex, the observed chemical shift δ^{obs} of an Ln-interacting nucleus is given by the sum of the diamagnetic term (δ^{dia}), which can be estimated from the La or Lu analogues, and of the paramagnetic contribution (δ para). The latter is the sum of the pseudocontact shift (PCS) and of the Fermi contact shift (FC). Because of their Ln-nuclei relative position dependency, the PCS values can be used to determine the solution structure of paramagnetic lanthanide complexes.

Table S1. The values of the chemical shifts are in ppm (CD₃OD, 400MHz or 100 MHz for the carbon) and the relaxation longitudinal time is in seconds.

N=N 6 4 3 N N N N N N N N N N N N N N N N N N	δ ^{1Η} La	$\delta^{ m 13C}$ La	T₁ La	δ ^{1H} Pr	δ ^{13C} Pr	δ ^{1Η} Eu	δ ^{13C} Eu	<i>T</i> ₁ Eu
2		149.87			146.09		153.59	
3	8.69	118.29	3.24	11.18	132.74	5.58	84.82	0.34
4		145.31			149.44		138.53	
5		144.13			146.87		140.01	
6	8.48	130.07	1.67	9.21	130.83	7.89	130.55	1.22
Tz		164.46			170.95		158.09	



Figure S9. Paramagnetic chemical shifts of the $[Pr(L_1)_3](Et_3NH)_3$ complex plotted vs. the Eu ones.

The good linearity of both proton and carbon atoms ($R^2 = 0.9$) is a proof of isostructurality between the two lanthanides. This is remarkable, considering that the L₁ system is highly conjugated with, a priori, a large extent of contact term at least on the pyridine ring (that is also affected by the partial positive pyridine nitrogen): this effect may be visualized for the C2 and C4 carbon atoms which lie moderately outside of the general linear trend. The slope of this plot can be used to assess the PCS of the nuclei considered.

	δ^{para} Eu	PCS Eu	FC Eu
Н3	-3.11	-4.09	0.98
	0.50	1 42	0.92
Нб	-0.59	-1.42	0.83
C2	-5.6	/	/
С3	-33.47	-12.94	-20.53
C4	3.72	/	/

Table S2. Separation of the PCS/FC terms from the total paramagnetic shift with the two lanthanides method.

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C5	-5.3	/	/
C6	0.48	-2.25	2.73
Tz	-6.37	-11.87	5.50



Figure S10. Comparison between the PERSES calculated solution structure of the $[Eu(L_1)_3]^{3-}$ anion and the XRD structure of the $Eu(PyTz)_3$ one.

The PCS values obtained for the Eu anion altogether with the longitudinal paramagnetic relaxation rates of H3 and H6 (2.66 ms⁻¹ and 0.22 ms⁻² respectively) were used to calculate the solution structure through the routine PERSEUS.

The structure has been calculated using as input a molecular mechanics optimized structure and imposing the following constraints: the Eu-N distances for the two tetrazole nitrogen atoms and the pyridine one were fixed respectively to 2.5 and 2.6 angstrom as found in the crystal structure of the Eu PyTz complex.

Table S3. Experimental and calculated (by PERSEUS) PCS shifts of proton and carbon atoms with the difference highlighted. C2, C4 and C5 are not reported due to some uncertainty on their assignment.

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	PCS exp	PCS calc	diff
H3	-4.09	-6.89	-2.80
H3	-4.09	-5.55	-1.46
H6	-1.42	-3.03	-1.61
C2	/	/	/
C3	-12.94	-10.82	2.12
C3	-12.94	-12.16	0.78
C4	/	/	/
C5	/	/	/
C6	-2.25	-2.96	-0.71
Tz	-11.87	-12.01	-0.14
Tz	-11.87	-11.55	0.32

The agreement factor of this structure defined as

AF (%) =
$$\sqrt{\frac{\sum_{i} (x_{i,\text{calc}} - x_{i,\text{exp}})^{2}}{\sum_{i} x_{i,\text{exp}}^{2}}} \times 100$$

is 16.7% considering just the PCS values.

Photophysical properties of the Eu/Tb complexes



Figure S11. Absorption, excitation, singlet (Gd complex), triplet (Gd complex -196°C) and emission spectra of [Eu(L₁)₃](Et₃NH)₃ in MeOH.



Figure S12 Excitation and emission spectra of $[Tb(L_1)_3](Et_3NH)_3$ complex in MeOH.



Figure S13. [Eu(L₁)₃](Et₃NH)₃ complex emission spectrum comparison MeOH/Solid state (above) and [Eu(L₂)₃](Et₃NH)₃ one (below).



Figure S14. [Gd(L₁)₃](Et₃NH)₃ complex singlet (black room temperature, red -196 °C) and triplet state (blue -196 °C) in solid state.

Table S4.	Singlet a	nd triplet l	levels of the	Gadolinium L	$_1$ and L_2 complexes.
	0	1			1 2 1

Li		$^{1}\pi\pi^{*}$	^c /cm ⁻¹	$^{3}\pi\pi^{*}/\text{cm}^{-1}$ (low T)		τ (s)
	-	max r.t.	max low T	0-phonon	max	_ (3)
L ₁	Solid	29760	29760	23100	18970	1.2(2)
	MeOH	28450	28800	23900	23900	2.05(0.2)
L_2	MeOH	28600	29200	24800	23200	1.85(0.1)

Calculation of the radiative lifetime.

The radiative lifetime τ_R of the Eu(⁵D₀) level is given by eq 1

$$k_{\rm r} = \frac{1}{\tau_{\rm r}} = A_{\rm MD,0} \cdot n^3 \cdot \left(\frac{I_{\rm tot}}{I_{\rm MD}}\right) \tag{1}$$

 $A_{\text{MD},0} = 14.65 \text{ s}^{-1}$ is the spontaneous emission probability of the ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{1}$ transition, *n* the refractive index of the medium, I_{tot} the ratio of the integrated total emission from the ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{J}$ transitions (J = 0-6), and I_{MD} the integrated emission of magnetic dipole transition ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{1}$.

The refractive index is assumed 1.5 for coordination complexes in solid state.

The total quantum yield Φ_{tot}^{Ln} obtained upon ligand excitation can be broken up into three contributions:

$$\Phi_{\text{tot}}^{\text{Ln}} = \eta_{\text{ISC}} \cdot \eta_{\text{ET}} \cdot \Phi_{\text{Ln}}^{\text{Ln}} = \eta_{\text{sens}} \cdot \Phi_{\text{Ln}}^{\text{Ln}} \qquad (2)$$

With

$$\Phi_{\rm Eu}^{\rm Eu} = \tau_{\rm obs} / \tau_{\rm r} \quad (3)$$

Where η_{ISC} is the efficiency of the intersystem crossing $({}^{1}\pi\pi^{*}\rightarrow{}^{3}\pi\pi^{*})$, η_{ET} the efficacy of the energy transfer $({}^{3}\pi\pi^{*}\rightarrow{}Ln)$, and Φ_{Ln}^{Ln} , the intrinsic quantum yield of the lanthanide ion (upon direct f-f excitation). The latter can be calculated from the observed luminescence lifetime τ_{obs} and the radiative lifetime τ_{r} which, in the case of Eu^{III} can be estimated using eq. (1) by assuming that the intensity of the purely magnetic dipole transition ${}^{5}D_{0}\rightarrow{}^{7}F_{1}$ is independent of the chemical environment:

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