Ln(III) complexes as potential phosphors for white LEDs

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Appendix A

The determination of photoluminescence quantum yields is of importance when studying luminescent compounds intended for use as a phosphor material. It is a measure of how efficient a compound is at converting light from one wavelength to another. In order to assess the quantum yields of many of the compounds described in this work, a setup based on an integrating sphere was built. This appendix gives a justification of the measurements, as well as a brief description of the required measurements.

Remarks on quantum yield determination

The photoluminescence quantum yield (PLQY) is an important performance benchmark for phosphor materials. It expresses how efficiently the phosphor can convert light to a different wavelength. Provided that the absorption at the excitation wavelength is high, a high PLQY phosphor material gives intense luminescence. The determination of the quantum yield requires only two quantities to be measured: the number of absorbed photons and the number of emitted photons per unit of time. Two principle methods for determining the PLQY exist: the *relative method* and the *absolute method* [1-3]. Both methods will be discussed below, with the focus on the second method.

The relative method for determination of PLQY

The relative method can be performed using standard emission and absorption spectrometers, but requires the use of a standard sample with a known quantum yied Φ_{Ref}. The absorption spectrometer is used for determining the absorption factors f_S and f_{Ref} of the sample and reference, respectively. The luminescence spectrometer is used to record emission spectra. The integrated intensities of the emission spectra, F_S and F_{Ref}, are readily obtained, and the PLQY of the sample, Φ_S, is obtained with equation A1.

$$\Phi_S = \frac{f_{Ref}}{f_S} \cdot \frac{F_S}{F_{Ref}} \cdot \Phi_{Ref} \qquad \text{(A1)}$$

This method is easily executed and provides a quick way for PLQY determination. Importantly, the emission spectrometer should be calibrated in such way that the intensity is proportional to the *photon flow*, i.e., $I(\lambda) \propto [mole\ of\ photons \cdot nm^{-1} \cdot s^{-1}]$ [3, 4]. Preferably, the excitation wavelength of the reference and sample is the same, otherwise an additional factor, correcting for the spectral intensity of the excitation source and differences in photon energy, is required in A1.The requirement for a standard sample with a known PLQY greatly limits the applicability of this method, especially when proper standards for the excitation wavelength of interest are lacking [3]. In addition, the method assumes an isotropic distribution of the emission intensity, which limits its usefulness for PLQY determination of, for example, luminescent films [1, 5, 6].

The absolute method for determination of PLQY

The absolute method does not rely on a reference sample with a known quantum yield, but on a spectrometer coupled to an *integrating sphere*. Also in this case, the setup must be calibrated to give intensities proportional to the photon flow. A detailed procedure for measuring absolute fluorescence quantum yields using a combination of an integrating sphere and a CCD spectrometer is given by De Mello *et al.* [1]. Using their method, three experiments as shown in Figure A1 are required for determining the PLQY of a compound. However, performing only two of the measurements can give the information needed for

determining the photoluminescence quantum yield, as will be demonstrated below. As in the original paper, it is assumed that the integrating sphere behaves as an ideal scatterer and does not absorb radiation. In addition, it is assumed that the compound under investigation has a large Stokes shift, so that it will not re-absorb its own emission. For the complexes described in this thesis, the Stokes shift is sufficiently large to make this a valid method of quantum yield determination. The three experiments are briefly described below and the following definitions will be used:

- L_x: relative number of unabsorbed excitation photons in experiment x.
- P_x: relative number of photoluminescence photons in experiment x.
- Φ: photoluminescence quantum yield of the sample under investigation.
- Abs_x: relative number of photons absorbed by the sample in experiment x.

The expressions for L_x, P_x and Abs_x for each experiment are listed in Table A1. Note that $L_x+Abs_x=L_a$ for all experiments.

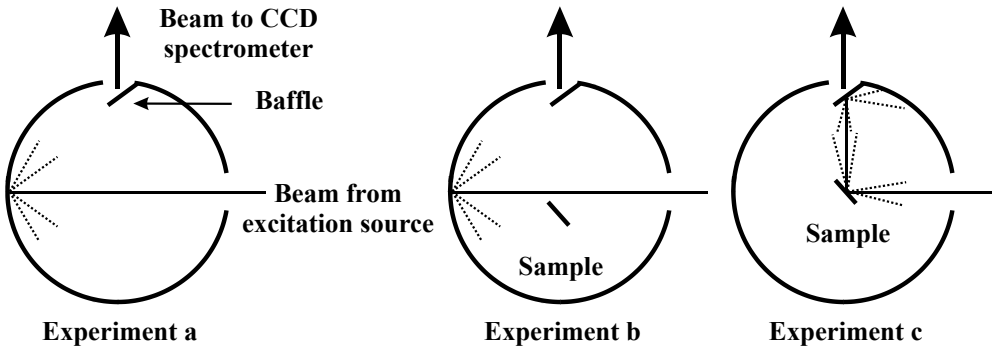

Figure A1: the three experiments described by De Mello for the determination of the PLQY of a luminescent sample [1].

Because of the way the spectrometer is calibrated, the relative number of photons is found by integrating the appropriate part of the spectrum.

Experiment a: The excitation beam is aimed at the wall of the empty integrating sphere. Only excitation source emission is measured by the CCD, its intensity is L_a.

Experiment b: The integrating sphere is loaded with a photoluminescent sample; the excitation beam is aimed at the sphere wall. A fraction μ of the excitation light scattered by the sphere wall is absorbed by the sample. With Φ as the photoluminescence quantum yield, the emission of the sample is given by $\Phi\mu L_a$. The intensity of the excitation signal is decreased to L_b.

Experiment c: The integrating sphere is loaded with a photoluminescent sample; the excitation beam is aimed directly at the sample. The sample absorbs a fraction A of the

incident light directly, a fraction (1–A) is transmitted or reflected into the integrating sphere. Of the latter fraction, a fraction μ is absorbed by the sample. Hence, the intensity of the excitation source is given by equation A2.

$$L_c = (1-\mu)(1-A)L_a = (1-A)L_b \quad \text{(A2)}$$

The number of absorbed photons in this experiment is determined by the number of photons absorbed at the first strike of the excitation beam with the sample (AL_a) and that fraction of excitation light that has not been absorbed at the first strike, but is scattered or transmitted into the sphere and absorbed at a later stage, resulting in equations A3.

$$Abs_c = AL_a + (1-A)Abs_b = AL_a + (1-A)\mu L_a \quad \text{(A3a)}$$

$$Abs_c = L_a\big(A + \mu(1-A)\big) \quad \text{(A3b)}$$

The sample emits light as a result from direct excitation (ΦAL_a) and as a result from excitation by the scattered or transmitted fraction of excitation light that has not been absorbed at the first strike ($\Phi\mu(1-A)L_a$), which results in equation A4 for P_c.

$$P_c = \Phi AL_a + \Phi\mu(1-A)L_a = \Phi AL_a + (1-A)P_b \quad \text{(A4)}$$

A summary of the experiments and the corresponding expressions is given in Table A1.

Table A1: Details of the luminescence experiments.

Experiment	a	b	c
Description	Empty I.S., exc. source on	Loaded I.S., exc. beam aimed at sphere wall	Loaded I.S., exc. beam aimed at sample
L	L_a	$L_b = (1-\mu)L_a$	$L_c = (1-A)L_b$
P	–	$P_b = \Phi\mu L_a$	$P_c = \Phi AL_a + (1-A)P_b$
Abs	–	$Abs_b = \mu L_a$	$Abs_c = \big(A + \mu(1-A)\big)L_a$

Calculation of the PLQY

From (A4), an expression for the photoluminescence quantum yield (A5) can be derived.

$$\Phi = \frac{P_c - (1-A)P_b}{AL_a} \quad \text{(A5)}$$

This expression is the same as equation 7 in De Mello's paper. However, on noting that P_c can be expressed as a function of L_a only, using $P_b = \Phi\mu L_a$, one finds equation A6.

$$P_c = \Phi AL_a + \Phi\mu(1-A)L_a = \Phi(AL_a + \mu(1-A)L_a) \quad \text{(A6)}$$

Equation A6 can be rearranged to give an expression for the quantum yield: equation A7.

$$\Phi = \frac{P_c}{L_a\left(A+\mu(1-A)\right)} \quad \text{(A7)}$$

Using this expression, the quantum yield can be determined from parameters measured in experiments a and c. The denominator of equation A7 can be recognized as the right-hand side of equation A3b: the absorbed light from the excitation source in experiment c. Intuitively, Abs_c is just the difference between L_a and L_c. Using the relations from Table A1 indeed it can be shown that $Abs_c = L_a - L_c$, see equations A8.

$$L_a - L_c = L_a - (1-\mu)(1-A)L_a \quad \text{(A8a)}$$

$$L_a - L_c = (\mu + A - \mu A)L_a = L_a\left(A + \mu(1-A)\right) \quad \text{(A8b)}$$

As a result, equation A7 simplifies to equation A9.

$$\Phi = \frac{P_c}{L_a - L_c} \quad \text{(A9)}$$

The three parameters in equation A9 are readily found from integrating the appropriate signals in the spectra resulting from experiments a and c.

Measurements in practice

In practice, experiment a is performed using a sample holder with optical grade $BaSO_4$ installed inside the integrating sphere as a white reference. This experiment results in the lower curve in Figure A2; its surface area is a direct measure of the number of excitation source photons that enter the integrating sphere over the integration time of the detector (L_a).

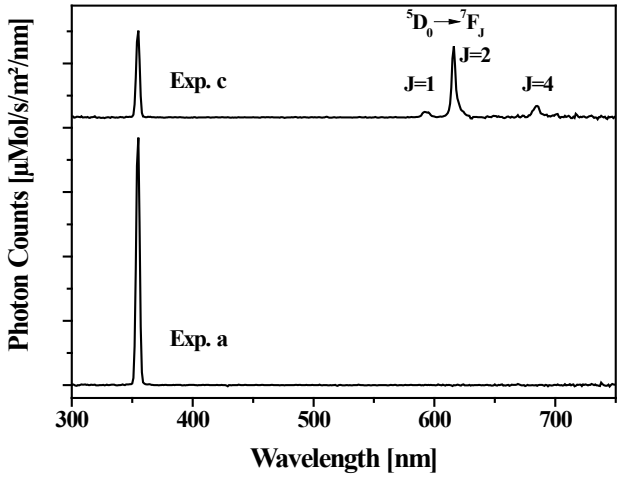

Figure A2: Spectra obtained with $BaSO_4$ (exp. a, bottom) and $[Eu(phen)_2(NO_3)_3]$ (exp. c, top) placed in the sample holder of the integrating sphere.

For experiment c, the sample holder is loaded with the compound of interest. The resulting spectrum contains a signal resulting from unabsorbed excitation photons and a signal from the luminescent compound. Integrating these curves gives L_c and P_c, respectively. A typical curve for experiment c performed on a luminescent Eu(III) complex, $[Eu(phen)_2(NO_3)_3]$ *in casu*, is shown on top in Figure A2.

Non-ideal behavior of the integrating sphere

Up until here, ideal behavior of the IS was assumed and it was assumed that its surface does not absorb radiation at any wavelength. In practice, integrating spheres tend to absorb radiation at shorter wavelengths. In view of the compounds described in this thesis, this means that short wavelength excitation photons are absorbed by the IS, which leads to an error in the PLQY determination. As the intensity of the excitation beam will be underestimated, an overestimation of the PLQY will result. To treat this problem, an additional absorption coefficient, *f*, has to be taken into account. Furthermore, it will be assumed that the excitation beam entering the IS has an intensity of L_i. A new set of equations, taking the additional absorption factor into account has been derived and is listed in Table A2. Not that the relation $L'_x+Abs'_x=L_i$ holds for each experiment.

Table A2: Set of equations describing the intensity of the excitation and emission signals.

Exp.	a	b	c
L'	$L'_a = (1-f)L_i$	$L'_b = (1-\mu)(1-f)L_i$	$L'_c = (1-A)(1-\mu)(1-f)L_i$
P'	$P'_a = 0$	$P'_b = \Phi\mu(1-f)L_i$	$P'_c = \Phi AL_i + (1-A)\Phi\mu(1-f)L_i$
Abs'	$Abs'_a = fL_i$	$Abs'_b = fL_i + \mu(1-f)L_i$	$Abs'_c = AL_i + (1-A)L_i\big(f+\mu(1-f)\big)$

From the expression for P'_c, in Table A2 an expression for the PLQY can be derived (A10).

$$\Phi = \frac{P'_c}{AL_i+(1-A)(1-f)\mu L_i} \qquad \text{(A10)}$$

Since $L'_c = (1-A)(1-\mu)(1-f)L_i$, one may write
$L'_c = (1-A)(1-f)L_i - \mu(1-A)(1-f)L_i$. This may be rearranged to give equation A11.

$$\mu(1-A)(1-f)L_i = (1-A)(1-f)L_i - L'_c \qquad \text{(A11)}$$

The left hand side of equation A11 can be recognized as the right part of the denominator in equation A10; substitution yields equation A12.

$$\Phi = \frac{P'_c}{AL_i+(1-A)(1-f)L_i-L'_c} \qquad \text{(A12)}$$

Equation A12 can be rearranged to give equation A13.

$$\Phi = \frac{P'_c}{L_i(1-f+Af)-L'_c} = \frac{P'_c}{L'_a-L'_c+AfL_i} \quad \text{(A13)}$$

This expression is similar to A9, but it contains an additional term in the denominator as a result from the absorption by the IS. This phenomenon can be corrected for only if the absorption coefficients of both the IS surface (*f*) and the sample (*A*) at the excitation wavelength of interest are known, as well as the intensity of the excitation beam.

References

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