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Tai-Sang Ahn, Rabih O. Al-Kaysi, Astrid M. Müller, Katherine M. Wentz, and Christopher J. Bardeen

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## Self-absorption correction for solid-state photoluminescence quantum yields obtained from integrating sphere measurements

Tai-Sang Ahn, Rabih O. Al-Kaysi, Astrid M. Müller,  
Katherine M. Wentz, and Christopher J. Bardeen  
*Department of Chemistry, University of California, Riverside, California 92521*

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A new method is presented for analyzing the effects of self-absorption on photoluminescence integrating sphere quantum yield measurements. Both the observed quantum yield and luminescence spectrum are used to determine the self-absorption probability, taking into account both the initial emission and subsequent absorption and reemission processes. The analysis is experimentally validated using the model system of the laser dye perylene red dispersed in a polymer film. This approach represents an improvement over previous methods that tend to overestimate the true quantum yield, especially in cases with high sample absorbance or quantum yield values. © 2007 American Institute of Physics. [DOI: 10.1063/1.2768926]

The absolute photoluminescence quantum yield (QY) of a material provides information about its potential for applications such as light-emitting diodes and solid-state lasers, as well as fundamental photophysical quantities such as its radiative lifetime. QY measurements on solid samples are complicated by the fact that the luminescence is typically not emitted in a uniform spatial pattern, but can be channeled in preferred directions due to waveguiding or nonuniform excitation of thick samples. To overcome the complicated geometrical factors inherent in solid-state photoluminescence measurements, and to avoid the need to use a fluorescence QY standard, integrating spheres are commonly used to measure solid-state QY's.<sup>1-8</sup> Spectral-based analysis methods have made this technique simpler and more accurate.<sup>9,10</sup> When an integrating sphere is used to measure quantum yields, the emitted light from even optically thin samples can be reabsorbed due to multiple reflections inside the sphere. This is especially true when the emission is only slightly shifted from the absorption, which is often the case for singlet exciton emission in organic semiconductors. Self-absorption (SA) competes with the escape of the luminescence from the specimen and changes the observed spectral shape, lifetime, and quantum yield from their true values.<sup>11,12</sup> The need for a quantitative analysis of how SA affects integrating sphere measurements has been recognized by previous workers, and a common approach is to correct the observed QY for SA effects by a simple scaling of the unattenuated luminescence spectrum to match the red wing of the observed spectrum.<sup>9</sup> In this note, we develop a more complete analytical model that quantitatively describes the effects of SA on both the luminescence spectral shape and the observed QY. We show that the commonly used SA correction method leads to an overestimation of the true QY, especially in cases of optically dense samples and/or high QY's. We apply our method to a model system consisting of the laser dye perylene red (PR) dispersed in the polymer polymethylmethacrylate (PMMA). We obtain a value for the solid-state QY from our corrected integrating sphere measurements that agrees with an independent estimate of the

QY based on photoluminescence lifetime measurements. The method presented in this article should significantly improve the accuracy of solid-state QY's obtained from integrating sphere measurements.

The theoretical basis of our method is summarized below.<sup>11,13</sup> Consider a fluorescent system with a quantum yield QY and where the probability of self-absorption of an emitted photon is  $a$ , so that  $1-a$  is the photon escape probability. The observed photoluminescence quantum yield  $QY_{\text{obs}}$  is given by a geometric series where the successive terms correspond to photon escape after successive absorption/reemission cycles,<sup>11</sup>

$$\begin{aligned} QY_{\text{obs}} &= QY(1-a)(1+aQY+a^2QY^2+\dots) \\ &= \frac{QY(1-a)}{1-aQY}. \end{aligned} \quad (1)$$

The self-absorption parameter  $a$  depends on the overlap of the absorption and emission spectra<sup>11</sup>

$$a = \int_0^{\infty} F(\lambda)[1-10^{-A(\lambda)}]d\lambda = 1 - \int_0^{\infty} F(\lambda) \times 10^{-A(\lambda)}d\lambda, \quad (2)$$

where  $F(\lambda)$  is the luminescence spectrum, in photons per wavelength, normalized to  $\int_0^{\infty} F(\lambda)d\lambda=1$ . The absorbance  $A(\lambda)$  depends on the chromophore's extinction coefficient  $\epsilon(\lambda)$ , its concentration  $[C]$ , and distance  $x$  through which the emitted photons must travel to escape the sample via the Beer-Lambert law,

$$A(\lambda) = \epsilon(\lambda)[C]x. \quad (3)$$

Because the sample sits in an integrating sphere, the emitted light can pass through the sample multiple times at different angles. Thus the path length  $x$  for reabsorption does not necessarily correspond to the film thickness and remains an undetermined parameter. To find  $a$ , and thus  $x$ , we consider the effect of the emission/reabsorption/reemission sequence on the observed luminescence spectrum. Since the reemitted fluorescence spectrum always begins with the true spectral

shape and then is attenuated by the absorption factor  $10^{-A(\lambda)}$ , as are all subsequent reabsorption/reemission events, we obtain another geometric series,

$$F_{\text{obs}}(\lambda) = F(\lambda) \times 10^{-A(\lambda)} + aQYF(\lambda) \times 10^{-A(\lambda)} + \dots$$

$$= \frac{F(\lambda) \times 10^{-A(\lambda)}}{1 - aQY}, \quad (4)$$

and from Eq. (2),

$$\int_0^{\infty} F_{\text{obs}}(\lambda) d\lambda = \frac{\int_0^{\infty} F(\lambda) \times 10^{-A(\lambda)} d\lambda}{1 - aQY} = \frac{1 - a}{1 - aQY}. \quad (5)$$

At first it appears that we have gained nothing—the unknown value  $a$  still appears in this expression, and we have no way to evaluate the absolute experimental quantity  $\int_0^{\infty} F_{\text{obs}}(\lambda) d\lambda$ . Now consider what occurs at the red edge of the luminescence spectrum where the sample absorption is negligible, i.e., the region where  $A(\lambda) \cong 0$ . The emission/reabsorption/reemission sequence still occurs, but this time without the spectral reshaping. For the long wavelength emission, we then obtain

$$F'(\lambda) = \frac{F(\lambda)}{1 - aQY} = \alpha F(\lambda). \quad (6)$$

The factor  $\alpha$  represents an empirical factor that scales the true spectrum  $F(\lambda)$  (obtained by measuring the luminescence in a dilute solution where it is not distorted by SA) to an enhanced spectrum  $F'(\lambda)$  whose red edge matches that of  $F_{\text{obs}}(\lambda)$ . Once  $\alpha$  [and thus  $F'(\lambda)$ ] is obtained by comparing the fluorescence spectra of the dilute sample with that of an optically dense sample, we can then combine Eqs. (5) and (6) to evaluate  $a$ ,

$$\frac{\int_0^{\infty} F_{\text{obs}}(\lambda) d\lambda}{\int_0^{\infty} F'(\lambda) d\lambda} = 1 - a \quad (7)$$

and then finally use Eq. (1) to obtain an expression for the QY,

$$QY = \frac{QY_{\text{obs}}}{1 - a + aQY_{\text{obs}}}. \quad (8)$$

It is straightforward to show that the earlier method of de Mello *et al.* leads to<sup>9</sup>

$$QY = \frac{QY_{\text{obs}}}{1 - a}. \quad (9)$$

It is worth noting that our expression for the QY in Eq. (8) cannot give a value greater than 1.0, in contrast to Eq. (9).

Experimental validation of the analysis presented above involves the preparation of  $10^{-3}M$  PR/PMMA film samples and the measurement of their photoluminescence lifetimes, which have been previously described.<sup>14</sup> UV-vis absorption spectra of the film samples were recorded with an Ocean Optics SD2000 absorption spectrometer while the absorption spectra of PR solutions were measured with a Varian Cary 50 UV-vis spectrophotometer. Absolute QY measurements of the films were conducted following the procedure described

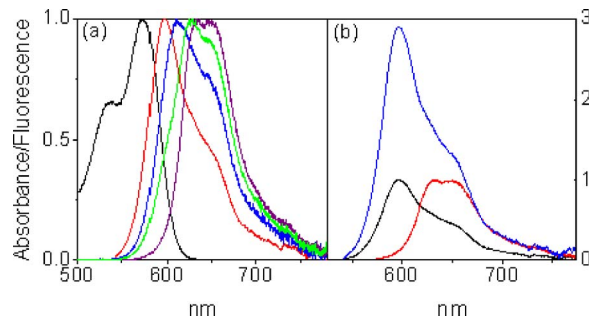


FIG. 1. (Color online) Normalized absorption (black) and true luminescence (red) spectra of  $10^{-3}M$  perylene red in PMMA films, along with the observed spectra obtained using the integrating sphere for films with maximum OD of 0.1 (blue), 0.3 (green), and 2 (purple). (b) Normalized true fluorescence spectrum  $F(\lambda)$  of  $10^{-3}M$  PR in PMMA films (black), the normalized observed luminescence spectrum  $F_{\text{obs}}(\lambda)$  of a film with maximum OD of 2.0 using the integrating sphere (red), and the scaled spectrum  $F'(\lambda)$  (blue) where the scale factor  $\alpha$  is adjusted so  $F'(\lambda)$  matches  $F_{\text{obs}}(\lambda)$  at  $\lambda = 680$  nm and longer.

by de Mello *et al.*,<sup>9</sup> using a Nd:YAG (yttrium aluminium garnet) laser output at 532 nm as the light source and a Lab-sphere Spectrafect integrating sphere connected to a calibrated Ocean Optics spectrometer through an optical fiber. All samples had surface areas of  $\sim 1$  cm<sup>2</sup>. The wavelength response of the integrating sphere was calibrated independently. After the wavelength correction was applied to the measured spectra, the  $QY_{\text{obs}}$  was subsequently determined using the relation

$$QY_{\text{obs}} = \frac{E_i - (1 - A)E_0}{L_e A}, \quad (10)$$

where  $A = (L_0 - L_i)/L_0$ .  $E_i$  and  $E_0$  are the integrated luminescence as a result of direct excitation and secondary excitation of the film, respectively.  $L_i$  is the measured laser signal when it directly hits the sample and  $L_0$  when it hits the sphere walls before hitting the sample.  $L_e$  is the laser signal when the sphere is empty and  $A$  gives the fraction of laser light absorbed by the sample. To obtain  $F(\lambda)$ , the experimental power spectrum was scaled by a factor proportional to  $\lambda$  in order to obtain a spectrum in terms of photon number. This scaling, although needed for mathematical consistency, had a negligible effect on the QY values.

The experimental absorption and unattenuated fluorescence spectra of PR are shown in Fig. 1(a), along with three emission spectra obtained from the integrating sphere measurements. As expected, the blue edge of the emission is progressively attenuated as the sample optical density increases. Figure 1(b) shows the experimentally measured  $F_{\text{obs}}(\lambda)$  along with the scaled unattenuated fluorescence spectrum  $F'(\lambda)$ . The scaling factor  $\alpha$  is adjusted so that the emission spectrum overlaps with that of  $F_{\text{obs}}(\lambda)$  for wavelengths greater than 680 nm, where there is no measurable sample absorption. For each sample thickness, we can calculate a value for  $\alpha$  and thus for  $a$  and then use Eq. (8) to evaluate the true QY from  $QY_{\text{obs}}$ . The results of these calculations are given in Fig. 2 for a range of peak sample absorbance values ranging from 0.1 to 2.0. In all cases, the  $QY_{\text{obs}}$  hovers around the value of 0.76, while applying the SA correction results in a larger value of 0.88. Perhaps surprisingly, there is not a strong dependence of  $QY_{\text{obs}}$  on the sample absorbance in

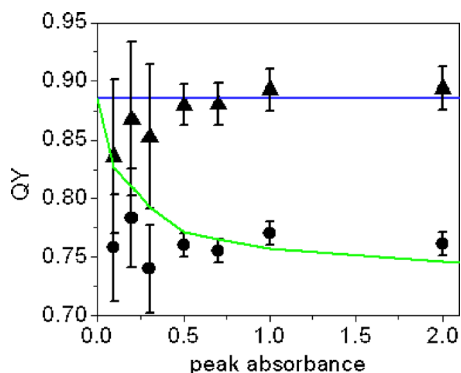


FIG. 2. (Color online) Observed quantum yields (circles), the recalculated quantum yields taking self-absorption into account (triangles), the QY from photoluminescence lifetime measurements (blue line), and the expected  $QY_{\text{obs}}$  predicted by Eqs. (7) and (8) with  $QY=0.88$  (green line). The higher errors at low OD samples are due to lower signals and the uncertainty in laser absorption  $A$  in Eq. (10).

Fig. 2. The reason of this lack of sensitivity is the high QY of PR. From Eq. (8), in the limit that  $QY \rightarrow 1.0$ , the  $QY_{\text{obs}}$  approaches the true QY, since multiple reabsorption events do not result in any net decrease in the number of detected photons. The small decrease in  $QY_{\text{obs}}$  predicted from Eq. (1) as a function of sample absorbance is thus close to the range of our experimental error, as shown by the calculated curve in Fig. 2. Finally, using Eq. (9) instead of Eq. (8) results in an unreasonably large QY value of  $\sim 200\%$ .

We can check our value for the QY by examining the photoluminescence lifetimes of PR in solution and in PMMA. Since the absorption and emission line shapes of PR in both dilute solution and in the polymer film are identical, any difference in the quantum yields between solution and solid must be due to different nonradiative rates, which also affect the observed fluorescence lifetimes

$$\frac{QY(\text{solution})}{QY(\text{PMMA})} = \frac{k_{\text{rad}}/[k_{\text{rad}} + k_{\text{nonrad}}(\text{solution})]}{k_{\text{rad}}/[k_{\text{rad}} + k_{\text{nonrad}}(\text{PMMA})]} = \frac{k_{\text{fl}}(\text{PMMA})}{k_{\text{fl}}(\text{solution})} = \frac{\tau_{\text{fl}}(\text{solution})}{\tau_{\text{fl}}(\text{PMMA})}. \quad (11)$$

We obtain single exponential decays for both PR in chloroform ( $5.96 \pm 0.04$  ns) and in optically thin (peak absorbance  $< 0.3$ ) PMMA films ( $5.50 \pm 0.03$  ns). Emission from thicker films is self-absorbed and displays longer lifetimes. Given a solution phase  $QY=0.96$ ,<sup>15</sup> Eq. (11) results in a  $QY=0.88 \pm 0.01$  for the PR/PMMA film. This value agrees with that obtained from the integrating sphere measurements to within the experimental error and provides an independent check on our SA correction method.

As shown in Eq. (3),  $a$  (and thus QY) could also have been obtained by calculating the spectral overlap of the absorption and emission spectra, along with an undetermined path length  $x$ . Figure 3 plots the  $a$  values obtained from our analysis of the integrating sphere data as a function of the sample's peak absorbance. Also shown are  $a$  values calculated using Eq. (3) and a value for  $x$  equal to the film thickness multiplied by a factor of 20. There is good agreement between the two curves. The factor of 20 enhancement in the effective path length likely depends on experimental details

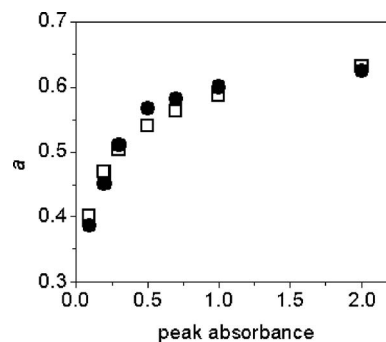


FIG. 3. Dependence of the self-absorption probability  $a$  on film absorbance for  $10^{-3}M$  perylene red in PMMA films.  $a$  can be calculated using Eq. (7) and the luminescence spectra from the integrating sphere (filled circles), or by using Eqs. (2) and (3) with  $x$ , the path length of travel for photon escape, set to the film thickness multiplied by a factor of 20 (open squares).

such as the number of round trips inside the sphere, sample size, detector aperture, etc. In principle, it is possible to use Eq. (3) and vary  $x$  to generate the attenuated fluorescence spectrum observed from the integrating sphere measurement. In practice, such a method would rely on knowing the long-wavelength behavior of the absorption to very high accuracy. In many solid-state samples, such measurements are often very challenging due to Fresnel effects and scattering. Our method based on scaling the true photoluminescence spectrum to match the red edge of the observed spectrum is both more convenient experimentally and also less prone to error. Of course, our method does depend on knowing the unattenuated emission line shape. This can usually be deduced by either changing the penetration depth of the exciting light by varying its wavelength, or by making an independent measurement in an ultrathin sample where SA does not play a role.

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