

Measurements of Solid-State Photoluminescence Quantum Yields of Films Using a Fluorimeter

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In this article we show that a commercial spectrofluorimeter can be used successfully in combination with an integrating sphere to measure solid-state photoluminescence quantum yields of films. This approach significantly simplifies the experimental method as the need for specialized equipment on the excitation and detection side is relaxed. Two different light-emitting polymer systems are examined with this approach, and the results agree with those that have been reported previously using different methods.

1. Introduction

Measurement of the absolute photoluminescence quantum yield (PLQY) of thin films is a more complex procedure than the corresponding solution measurement. This is due to the fact that films are a high refractive index medium, which in turn results in substantial waveguiding of the luminescence. To overcome the angular dependence of the emission from films, integrating spheres are generally used to collect the emitted light. The use of integrating spheres has usually required a laser as the excitation source in combination with a fiber-coupled charge coupled device (CCD) camera or a calibrated photodiode as the luminescence detectors.^[1,2] The experimental equipment required for both of these approaches is expensive and not commonly available in most laboratories. Secondly, the usage of lasers as excitation sources usually represents a limitation since one cannot freely choose the excitation wavelength in the UV and visible parts of the electromagnetic spectrum.

In this article we show that a commercial spectrofluorimeter in combination with an integrating sphere can be used with success to determine the solid-state PLQY of films. This approach has great advantages as it reduces the need for bulky and expensive equipment such as laser excitation sources and instead utilizes a basic spectrometer found in most laboratories. In addition this means that the excitation

wavelength can freely be chosen in the 300–600 nm range of the spectrum. There is also no need for an independent detection system since the internal luminescence monochromator and photodetector of the fluorimeter can be used to record the luminescence. In the case of our fluorimeter, which has a photon counting detection systems, very sensitive measurements can be made, allowing very low PLQYs to be measured accurately.

2. Results and Discussion

To realize this simple approach, a PTFE-coated integrating sphere (Glen Spectra) was mounted into a Jobin Yvon Horiba Fluoromax-3. The entry and output ports were in a perpendicular angle configuration (in the spectrometer plane), which meant that the design geometry of the fluorimeter was also used in the integrating sphere measurements. The sample material was spin-coated onto a 10 mm diameter quartz substrate and mounted about 20 mm into the sphere from a holder in the entry port facing the excitation light beam. The measured spectra were background corrected by subtracting the spectrum obtained using a blank substrate and subsequently corrected for the wavelength sensitivity of the fluorimeter and the spectral response of the sphere. The spectral response of the sphere was determined using a calibrated tungsten lamp (Ocean Optics) and the fluorimeter as the detector. The spectral correction factor of the fluorimeter was also obtained using the calibrated tungsten lamp. These two normalization curves were then used to correct the recorded luminescence spectrum of the sample. This correction is applied to all subsequently measured emission spectra in the measurement of the sample PLQY.

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The PLQY was subsequently determined according to the method outlined by de Mello.^[1] In this approach the PLQY (Φ_{PL}) is given by

$$\Phi_{\text{PL}} = \frac{E_i(\lambda) - (1-A)E_0(\lambda)}{L_c(\lambda)A} \quad (1)$$

where

$$A = \frac{L_0(\lambda) - L_i(\lambda)}{L_0(\lambda)} \quad (2)$$

According to this notation $E_i(\lambda)$ and $E_0(\lambda)$ are, respectively, the integrated luminescence as a result of direct excitation of the film and secondary excitation. The latter emission is due to reflected excitation light from sphere walls hitting the sample, which in turn is not directly in the path of the excitation beam.^[1] A is the film absorbance, which is found by measuring the integrated excitation profiles, i.e., the emission signal measured across the excitation wavelength (± 5 nm), for two situations as follows: $L_i(\lambda)$ is the integrated excitation when the film is directly excited and $L_0(\lambda)$ is the integrated excitation when the excitation light first hits the sphere wall as previously explained. $L_c(\lambda)$ is the integrated excitation profile for an empty sphere.

We have measured the PLQY of the light-emitting polymer poly(2,5-pyridinediyl) (PPY) as a demonstration of this approach. PPY was synthesized and characterized as previously described in the literature.^[3] Films were spin-coated on a circular disc, and the film thickness was about 200 nm.

Figure 1 shows the luminescence spectrum of PPY upon excitation at 370 nm. This particular example is chosen as PPY requires UV excitation, which is difficult to obtain and carries many problems with secondary emission, for instance from (detector) blocking filters used with laser excitation. The sharp lines to the left are the excitation profiles $L_i(\lambda)$ and $L_0(\lambda)$ as defined previously. From these two lines the film absorption can be calculated according to the relation for A above. There is generally a large difference in intensity between the luminescence of the film and the excitation lines. It is therefore very important to ensure that the detected signal intensities are still within the linear range of the photomultiplier tube of the fluorimeter. In order to insure that this was achieved, neutral density filters were used to attenuate the intensity of the lamp profiles.

From the experimental results we obtained a PLQY for the PPY film of $\Phi_{\text{PL}} = 18 \pm 2\%$. Using the method outlined by Greenham et al.^[2] and excitation at 360 nm from a continuous wave Ar-ion laser, the PLQY was found to be 20%.^[4] Similar measurements on a polyfluorene polymer, poly(9,9-di(ethyl-

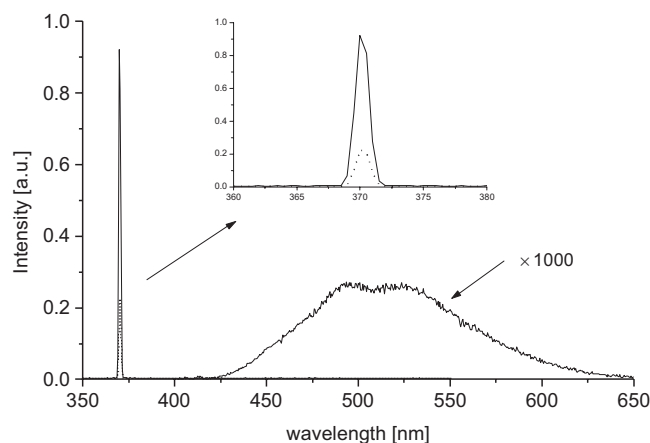


Fig. 1. Photoluminescence of PPY upon excitation at 370 nm. Inset: Magnification of the excitation lines. The solid line gives the L_0 while the dashed line gives the L_i parameter.

hexyl)fluorene), gave a PLQY of $\Phi_{\text{PL}} = 24 \pm 1\%$,^[5] which is in excellent agreement with what has been reported by Virgili et al.^[6]

3. Conclusions

The results are rewarding since they show that PLQYs can be determined in an easy way with an instrument that has additional flexibility compared to the experimental set-ups that are generally used, and will be found in very many laboratories. This should make PLQY measurements accessible to a large number of groups with the minimum of cost. We also remark that there is scope for improvements, especially on the detection side as the dark count of the photomultiplier tube can be reduced with a simple cooling device. This would improve the sensitive of the experiment.

- [1] J. C. de Mello, H. F. Wittmann, R. H. Friend, *Adv. Mater.* **1997**, *9*, 230.
- [2] N. C. Greenham, I. D. W. Samuel, G. R. Hayes; R. T. Phillips, Y. A. R. Kessener, S. C. Moratti, A. B. Holmes, R. H. Friend, *Chem. Phys. Lett.* **1995**, *241*, 89.
- [3] T. Yamamoto, T. Murayama, Z.-H. Zhou, T. Ito, T. Fukuda, Y. Yoneda, F. Begum, T. Ikeda, S. Sasaki, H. Takezoe, A. Fukuda, K. Kubota, *J. Am. Chem. Soc.* **1994**, *116*, 4832.
- [4] A. P. Monkman, L.-O. Pålsson, R. W. T. Higgins, C. Wang, M. R. Bryce, A. S. Batsanov, J. A. K. Howard, *J. Am. Chem. Soc.*, in press.
- [5] C. Rothe, L.-O. Pålsson, A. P. Monkman, *Chem. Phys.*, in press.
- [6] T. Virgili, D. G. Lidzey, D. D. C. Bradley, *Adv. Mater.* **2000**, *12*, 58.