Chemical Physics Letters 506 (2011) 321–325

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Measuring external photoluminescence quantum efficiency of organic solid films

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ARTICLE INFO

Article history:
Received 20 January 2011
In final form 12 March 2011
Available online 16 March 2011

ABSTRACT

An algorithm with high reliability to obtain the photoluminescence quantum efficiency (PLQE) of the organic solid materials was developed by directly calculating the number of the absorbed photons and the emitted photons. By eliminating the step to determine the sample's absorbance, not only is the experiment simplified, but also the PLQE value is less error-prone. Moreover, our developed method could be extended to more fluorescent materials, for which current methods either fail or require performing complex calculations. Three conjugated polymers and a dendrimer were tested to demonstrate the method's advantages of easier set-up, fewer steps for processing, and higher accuracy.

1. Introduction

The absolute external photoluminescence quantum efficiency (PLQE) is one of the most important parameters to characterize organic fluorescent materials, due to the materials' applications in organic light emitting diodes (OLEDs) [1–3]. Achieving high PLQE is critical for OLEDs to be successfully employed in flat-panel displays and solid-state lighting [4–6]. In addition, the study of the luminescence properties of conjugated molecules and polymers would contribute to understanding the mechanism of radiative decay of singlet excitons [7,8]. Though the PLQE measurements become a routine work in optical assessments of the luminescent materials, it is more difficult to accurately determine the materials' PLQE in solid-state than in solution, because of the waveguiding of the luminescence and the angular dependence of the emission [9–11]. For example, the reported PLQEs of poly(9,9-dioctylfluorene) (PFO) [12–14], which is an important conjugated polymers in polymer OLED applications, vary from 46% to 80% [15–19].

Greenham et al. established a widely adopted technique [20] to measure the PLQE with an integrating sphere by modeling $\eta = \frac{P_{\text{sample}}-(1-A)P_{\text{back}}}{A\times L}$, where L is the total amount of the excitation laser photons into the sphere, A is the sample's absorbance upon direct laser incidence, P_{sample} is the total amount of PL emission photons from the sample, and P_{back} is the PL emission photons caused by the absorption of the scattered laser light. Based on Greenham's algorithm, de Mello et al. improved the technique by introducing an optical-fiber-linked CCD spectrometer and calculating the absorbance A through multi-stepped experimental configurations [21]. de Mello's method avoids the determination of the sample's reflectance and transmittance outside the integrating sphere, leading to less experimental errors. Several other groups reported further modifications [22–25] by modifying the experimental apparatus, i.e. spectrometer, while keeping the experimental set-up and the algorithm developed by de Mello intact.

In this contribution, we designed a reliable and reproducible method to determining the PLQE of organic solid films, by deriving the absorbed laser photons and the PL emission photons with a simple two-stepped measurement. The experiment set-up merely employs an integrating sphere, a filter, and a photodiode, which are easily available in most laboratories. No special spectrometer is required. The PLQE value is easily calculated with three direct readings and two pre-calculated parameters without the need to know anything about the reflectance and the transmittance, leading to reliable measurements even for highly light-scattering films. Organic samples with red, green and blue emission colors, i.e. widely investigated conjugated polymers including poly[2-methoxy,5-(2-ethylhexoxy)-1,4-phenylenevinylene] (MEH-PPV) [20,26], poly[2-(4-(3′,7′-dimethyloctyloxy)-phenyl)-*p*-phenylenevinylene] (P-PPV), poly(9,9-dioctylfluorene) (PFO), and a blue fluorescent conjugated dendrimer (G0) [27] were tested to compare our method's measurement results with those done by the other two methods mentioned earlier. The materials' chemical structures are illustrated in Figure 1. Dependence of the PLQEs on pure glass and ITO-coated glass substrates was also studied to reveal that the conductive coating had a significant quenching effect on the PLQE.

2. Experimental

The experiment set-up and the measurement steps are schematically illustrated in Figure 2. The integrating sphere (Labsphere

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doi:10.1016/j.cplett.2011.03.039

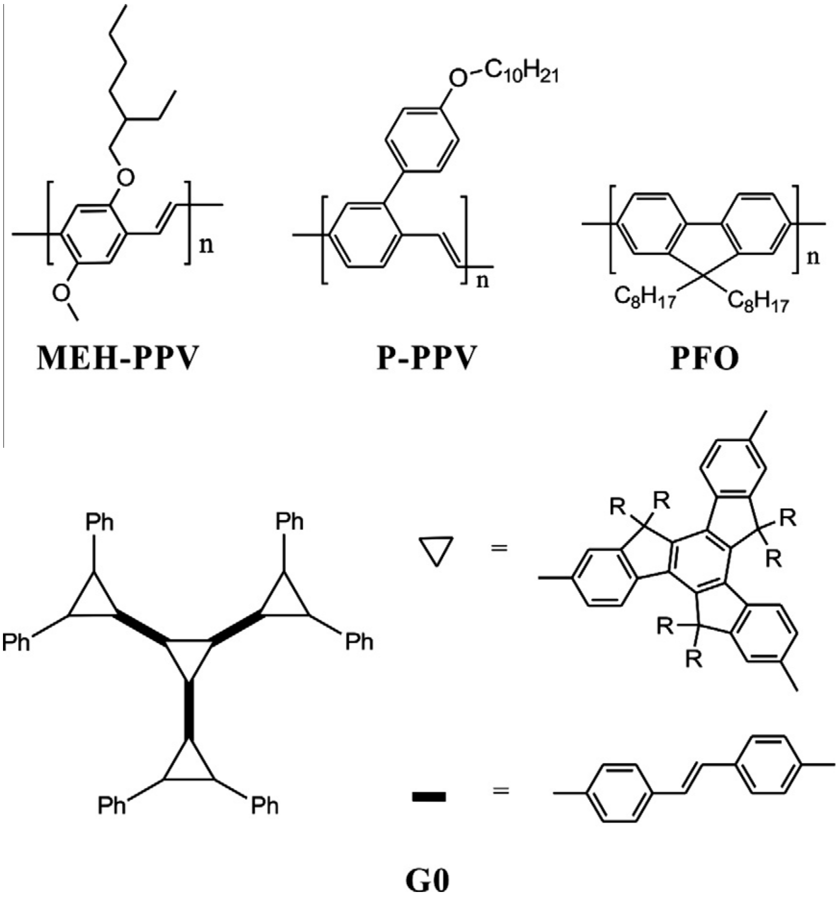

Figure 1. Chemical structures of MEH-PPV, P-PPV, PFO and G0.

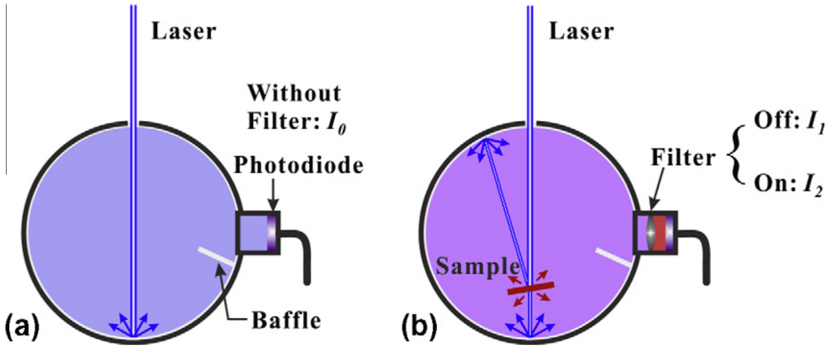

Figure 2. Schematic illustration of the PLQE measurements. (a) No sample is inside the integrating sphere. The photodiode reading is recorded as I_0 (without filter). (b) The sample is in place, and the laser is incident on the sample. With the filter off and on, the photodiode readings are recorded as I_1 and I_2, respectively.

Inc.) coated with diffusely reflecting material (barium sulfate) has an exit port for the placement of a photodiode (UDT, S370) and a filter. A tiny aperture on the sphere allows the import of an excitation laser beam. The amount of light received by the photodiode is proportional to the total amount of light inside the sphere with the proportionality constant φ equaling $\Omega/4\pi$, where Ω is the solid angle projected by the photodiode [21,28].

In the first step, no sample is present inside the sphere, as shown in Figure 2a. The radiation flux from the diffusely distributed laser light is collected by the photodiode. If the total amount of laser photons in the sphere is L_a, the light intensity recorded by the photodiode I_0 (without the filter), can be expressed as:

$$K(\lambda_{ex})\Phi L_a = I_0$$

where $K(\lambda) = \frac{S_{\text{Sphere}}(\lambda)}{S_{\text{Lamp}}(\lambda)} G(\lambda)$ is the photoelectric response of the system, in which $\frac{S_{\text{Sphere}}(\lambda)}{S_{\text{Lamp}}(\lambda)}$ is the spectral response of the sphere acquired by using a tungsten-halogen calibration lamp as described in Ref. [20], and $G(\lambda)$ is the monochromatic incident photon-to-electron conversion efficiency (provided by the manufacturer). λ_{ex} is the excitation wavelength. Thus,

$$L_a = \frac{I_0}{\Phi K(\lambda_{\text{ex}})} \tag{1}$$

In the second step, the laser light is incident on the sample inside the sphere, while no laser beam is reflected directly through either the import hole or the photodiode as demonstrated in Figure 2b.