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Absolute photoluminescence quantum yield of perylene dye ultra-thin films

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Using integrating sphere method we have determined the absolute photoluminescence quantum yield (QY) of two perylene derivatives in ultra-thin films. Monomolecular and multilayer films were deposited onto quartz substrates by using Langmuir–Blodgett technique. The method adopted by us allows to evaluate QY with a high accuracy for samples having absorbance down to 0.01. The evaluated luminescence quantum yield of mono- and multilayers of two 3,4,9,10-tetra-(n-alkoxy-carbonyl)-perylenes was in the range of 7–12%.

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1. Introduction

Prospect of creating low cost, energy-saving and flexible optoelectronic devices is one of the driving forces behind thin film technology development, i.e. spin-coating, molecular beam epitaxy, self-assembly. One of the key parameter for such structures is their QY defined as the efficiency of absorbed to emitted photon conversion [1]. QY reflects competition between radiative and non-radiative processes, therefore it is the most important and suitable parameter to characterize the material's luminescence usefulness. However, the exact evaluation of this parameter for thin films on solid substrates is complicated, mainly due to scattering, anisotropy of angular emission and wave-guide effect. These difficulties can be overcome by using integrating sphere (IS) method [2–4]. In the case of nanometer luminous structures low brightness (absorbance·QY) causes additional difficulties resulting from limited dynamic range of the detector [5]. To authors best knowledge there are no data on QY of organic dye ultra-thin films (single nanometer thick) using integrating

sphere method. On the other hand, taking advantage of more sensitive lifetime measurement methods require theoretical assumptions to extract absolute quantum yield value [6,7]. Moreover, in the case of applications in organic optoelectronic devices it is better to directly measure the efficiency of photon emission than fluorescence lifetime, which is rather useful in fundamental research.

In this paper we report our results on absolute photoluminescence quantum yield of two perylene dye films with varying thickness (dye molecular structures shown in Fig. S1 ESM). Langmuir–Blodgett deposition technique gave us possibility to control thickness with single nanometer precision by simple multiplication of the deposition process. This way, the amount of light absorbed and then emitted by the structure can be easily increased. The results of QY ranged from 7% to 12% and were consistent for both excitation wavelengths, 443 nm and 472 nm, used in experiment.

2. Experimental

We utilized polytetrafluoroethylene (PTFE) integrating sphere (90 mm in diameter) coupled with a 3 mm optical fiber to our homemade photon-counting spectrofluorimeter

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[8]. The sample was placed in the center of the IS in PTFE holder, which also served as a baffle, preventing direct illumination of the output port situated below (see schematic drawing in Fig. 1). At the excitation port (light source), located perpendicularly to the output port, 443 nm (300 mW) interchangeably with 472 nm (60 mW) blue laser diode was used. To prevent saturation of the detector the excitation source output power was adjusted with a neutral density filter. The tungsten lamp (standard illuminant A, 6067C/05, Philips, Germany) was used in the calibration procedure. The obtained response curves of the entire system (detector, monochromator, IS, etc.) were applied to all measured spectra, which were then background corrected with subtracting the spectrum when a blank was present at the sample position. A cuvette filled with a solvent was used as the blank in the case of solution measurements, whereas for the thin films, a substrate was used. The final value of QY was calculated using equation:

$$QY = \frac{N_E}{N_A} = \frac{L_{SAMPLE} - L_{BLANK}}{E_{BLANK} - E_{SAMPLE}}, \qquad (1)$$

where E_{SAMPLE}, E_{BLANK} – sample and blank integrated spectra of excitation beam, respectively; L_{SAMPLE} – integrated spectra in the sample's luminescence wavelength range when the sample or L_{BLANK} – if a blank was inside the IS.

It should be noticed that although, the L and E spectra are measured under the same experimental conditions, the number of emitted photons N_E is determined with very different accuracy than the number of absorbed photons N_A. Due to the fact, that the sample absorbs only about 2% of incident light, the instability of the excitation source output power is the key issue in measurement of E spectra, thus the number of absorbed photons. By contrast, the number of emitted photons is the product of the intensity of incident light, the absorbance of the sample and its quantum yield. Instability of the excitation light power of 1% would cause 50% change in calculated number of absorbed photons, and only about 0.02% change in the number of emitted photons, assuming QY = 100%. For this reason, we have measured excitation spectra 10 times for each sample (E_{SAMPLE}) and a corresponding blank (E_{BLANK}). The signal was measured 2 times in sample's luminescence range (L_{SAMPLE} and L_{BLANK}). The standard deviation of the QY results obtained from 10 independent excitation spectra measurements served as the experimental error.

Another experimental problem arises from the difference in excitation and emission signal intensities [5,9]. Small absorbance of the sample in conjunction with broad emission spectrum (compared to excitation) results in excitation to emission spectrum intensity ratio exceeding linear range of the detection system (the number of recorded photo counts, 10^2–10^6 cps). To avoid saturation of the photomultiplier, a neutral density filter with optical density OD = 1.8 at excitation wavelengths was used to attenuate the intensity for excitation signal measurements. This filter was applied in calibration procedure, therefore the correction for its attenuation is included in the response curves.

3. Results and discussion

To validate the performance of the system, the absolute quantum yield of the 0.1 M NaOH fluorescein solution was evaluated. Fluorescein is one of three well established fluorescence standards recommended by IUPAC (International Union of Pure and Applied Chemistry) [10]. The concentration of fluorescein in the solution was adjusted to match the absorbance value of studied monolayers (ABS = 0.01) at the excitation wavelength (472 nm). To exclude sample size effect, quartz cuvettes with 1 cm and 0.1 cm path length were used. The obtained QY = 91% (Table 1) is in good agreement with most credible literature values [11,12] (Porres et al. QY = 0.91, Magde et al. QY = 0.92), indicated in technical report by IUPAC [10].

We chose to investigate mono- and multilayer Langmuir–Blodgett films of 3,4,9,10-tetra-(propyloxy-carbonyl)-perylenes (P1) and 3,4,9,10-tetra-(octyloxy-carbonyl)-perylene (P2). The preparation method, formation and spectroscopic characterization of the films are described in detail in Electronic Supporting Material (ESM). Both dyes possess high fluorescence quantum yield in diluted solution evaluated using relative method ($\sim$80%) [13]. However in closely-packed structures aggregation of perylene molecules occur [14–23], which is usually detrimental for the luminescence efficiency.

Obtained results are gathered in Table 1. For comparison we have investigated two samples of LB films with the same number of layers. The number by the name represents multiplicity of dipping cycles (LB1-4). As it can be seen there are only small differences of the QY value between samples of the same type, what we interpret as a slightly different molecular organization from sample to sample. The results for both excitation sources are also consistent, which implies that the QY is not wavelength dependent.

In the case of both dyes, P1 and P2, absolute quantum yield in condensed films is lower than in diluted solution, as it is usually observed [1,18,24]. Spectroscopic studies (Figs. 2 and 3) show broadening and batochromic shift of the absorption spectra. In connection with structureless band observed in the emission spectra, this clearly indicates self-aggregates formation of the dye molecules, which results in lowering QY with the maximum value of 12% for P1 and 9% for P2 monolayers.

The QY of P1 (the dye with 3 carbon atoms in substituted alkyl chain) multilayer structures decreases with the number of layers from 12% for a monolayer (P1 LB1) to 7% for 4-layer film (P1 LB4). At the same time the emission spectrum (Fig. 2) changes drastically. As the number of layers increases, the intensity of the peak related to the genuine excimer emission ($\lambda_{MAX} \approx 610$ nm) increases significantly with respect to the intensity of the band connected with monomer fluorescence. We find this a consequence of molecular interaction between adjacent layers or different organization in subsequent layers of P1. QY values obtained for the sample excited at different wavelengths are very close to each other but not identical, due small shift of the sample location and its non-uniformity.