Journal of Luminescence 166 (2015) 215–221

Contents lists available at ScienceDirect

Journal of Luminescence

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

Long-lived and largely red-shifted photoluminescence of solid-state rhodamine dyes: Molecular exciton coupling and structural effect

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ARTICLE INFO

Article history:
Received 15 February 2015
Received in revised form
29 April 2015
Accepted 21 May 2015
Available online 30 May 2015

Keywords:
Solid-state rhodamine
Fluorescence
Absorption
Exciton coupling
J aggregate

ABSTRACT

The optical absorption and fluorescence properties of five rhodamine dyes in solid-state are measured and show large difference from that in their gas phase or liquid solvents. All solid-state rhodamine dyes strongly absorb all light in UV and visible region, but emit only red and NIR fluorescence (680–800 nm, > 100 nm red-shifted from that in solution). Further more, the absorption maxima of a solid-state rhodamine show a large red-shifted band (~100 nm) and blue-shifted peak (~125 nm) compared to that in solutions, indicating a strong molecular exciton coupling between molecules. All solid-state rhodamines still show reasonably good fluorescence quantum yield (Φ_f). In particular, solid-state Rhodamine B butyl ester and sulfonyl Rhodamine B showed a much longer emission lifetime (τ_f) than that of the corresponding molecular rhodamine, i.e. 4.12 and 4.14 ns in solid state compared to 1.61 and 2.47 ns in solution. The chemical structure of a rhodamine molecule showed dramatic effect on Φ_f and τ_f values for solid state rhodamine. The larger substituent in the benzene moiety favors higher Φ_f and τ_f values of rhodamine solids. These effects can be elucidated by the relation between structure-molecular distance and molecular exciton couplings.

1. Introduction

Rhodamine dyes and their derivatives (Fig. 1) are widely used in diverse areas for research and commercial purposes due to their excellent fluorescence properties [1–6]. The fluorescence properties of rhodamines are mostly reported in liquid-phases, in which a rhodamine molecule is isolated by surrounding water or organic solvent molecules. Such studies have been the subject of many investigations over last 50 years [7–18]. Only recently literature on gas-phase rhodamine fluorescence became available [19–24]. The emission of isolated molecular rhodamine dyes in gas-phase reveals quite different properties from that in liquid-phase. For example, the fluorescence lifetime of rhodamine 6G (R6G) in gas-phase is 5.87 ns, significantly longer than 3.96 ns in ethanol solution. Knowledge of the intrinsic lifetimes of rhodamines will aid the development of fluorescence probe of gaseous ions. It also helps to better understand interactions between solvent and fluorescent dye molecules.

Solid-state rhodamine dyes represent another form of these substances in which a rhodamine molecule has a fixed site and is closely surrounded by other rhodamine molecules. The overlap of electron cloud of the neighboring dye molecules may lead to strong exciton coupling and alter the optical emission and absorption properties of rhodamine materials. Depending on the relative orientation of dye molecules, either H-type or J-type exciton-coupling can occur, which can give different optical properties for a solid-state rhodamine dye.

Solid-state rhodamine dyes have found application as fluorescence probes to monitor the dispersion of cyclodextrins in polymeric nanocomposites [25]. Thin films of rhodamine 6G dispersed in titanium dioxide was used in organic solar cell [26]. These applications are directly based on the photophysics of solid-state rhodamines, but the fluorescence properties of rhodamine solids have never been reported to the best of our knowledge.

Based on above considerations, hereby we report the optical absorption and fluorescence properties of five solid-state rhodamine dyes based on our previous experience in elucidating the fluorescence mechanism of rhodamine and fluorescein dyes in solution [18,27–33]. Indeed, these solid-state dyes show very different optical absorption and fluorescence properties from that in gas phase or liquid solvents.

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http://dx.doi.org/10.1016/j.jlumin.2015.05.048
0022-2313/

2. Experimental section

2.1. Reagents and apparatus

Rhodamine dyes were purchased from Beijing Chemical Reagents Ltd. including Rhodamine B (RB), Rhodamine B ethyl ester (Et-RB), Rhodamine B butyl ester (But-RB), Lissamine Rhodamine (LA-RB), Sulfonyl Rhodamine B (Sulfo-RB). The purity of these rhodamines was stated to be better than 97%. Acetonitrile is of analytical grade and used as received.

XRD spectra were recorded on Rigaku D/max-2500/PC X-ray diffractometer. The particle images of rhodamine solids were recorded on TS4 digitized optical microscopy of Aikexue Inc. The UV–visible absorption spectra of rhodamine solids were obtained using a Hitachi U-4100 UV/VIS/NIR spectrophotometer. The absorption spectra of rhodamine in solution were recorded on a stellarNet Black Comet BLK-CXR-SR fiber optic spectrometer using 1 cm matched quartz cuvettes. Fluorescence measurements were performed by using a FLS 920 fluorospectrometer of Edinburgh Instruments.

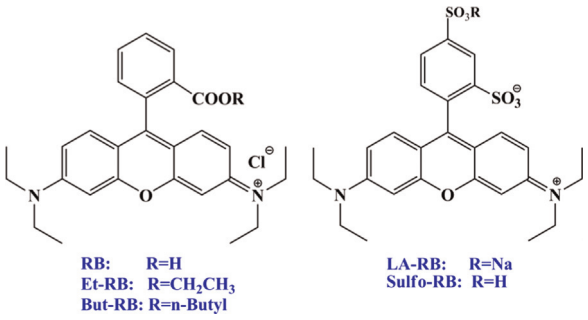

Fig. 1. Chemical structures and abbreviations of rhodamine dyes in this report.

2.2. Photophysical measurements

2.2.1. Fluorescence spectra

Fluorescence spectra were recorded with excitation at 480 nm (20 °C). The emission and excitation slits were both 1.0 nm. The fluorescence was measured at 90° to the incident excitation beam. The fluorescence intensity at all wavelengths was calibrated against the detector response and the excitation light intensity.

2.2.2. Fluorescence quantum yields

Fluorescence quantum yield (Φ_f) in solutions was measured by using $\phi_f^0 = \left(F_S \cdot A_0 \cdot n_S^2\right) / \left(F_0 \cdot A_S \cdot n_0^2\right)$, in which F is the integrated fluorescence intensity, A is the absorbance at excitation wavelength, n is the refractive index of the solvent used, the subscript 0 stands for a reference compound and s represents samples. R6G in ethanol was used as the reference ($\phi_f^0 = 0.95$) [11]. Φ_f of samples in solid state was measured by using an integrating sphere.

2.2.3. Fluorescence lifetimes

Measurements of the fluorescence lifetimes were performed with standard time-correlated single-photon counting method. The excitation light was a portable diode laser (EPL-375, Edinburgh Instruments), laser beam was guided into the samples, and fluorescence (the wavelength at the emission maximum of a dye) was detected with a PMT (Hamamatsu R928) cooled to −21 °C. The repetition rate is 10 MHz whilst the count rate did not exceed 20 kHz (0.2%) in order to avoid pile-up effects. The bandwidth for excitation as well as for emission was <2 nm. The prompt response function of the system had an fwhm is less than 700 ps. The convolution method was used to fit the $I(t) = A + Be^{(-t/\tau f)}$ or $II(t) = A + B_1 e^{(-t/\tau f1)} + B_2 e^{(-t/\tau f2)}$ to obtain the fluorescence lifetime.

3. Results and discussion

Optical microscope images revealed that the as-purchased rhodamine solids mainly consist of shiny sheets with the size of $50(\pm 40) \times 35(\pm 20)\ \mu m^2$ (Fig. 2). Some sheets are rectangular

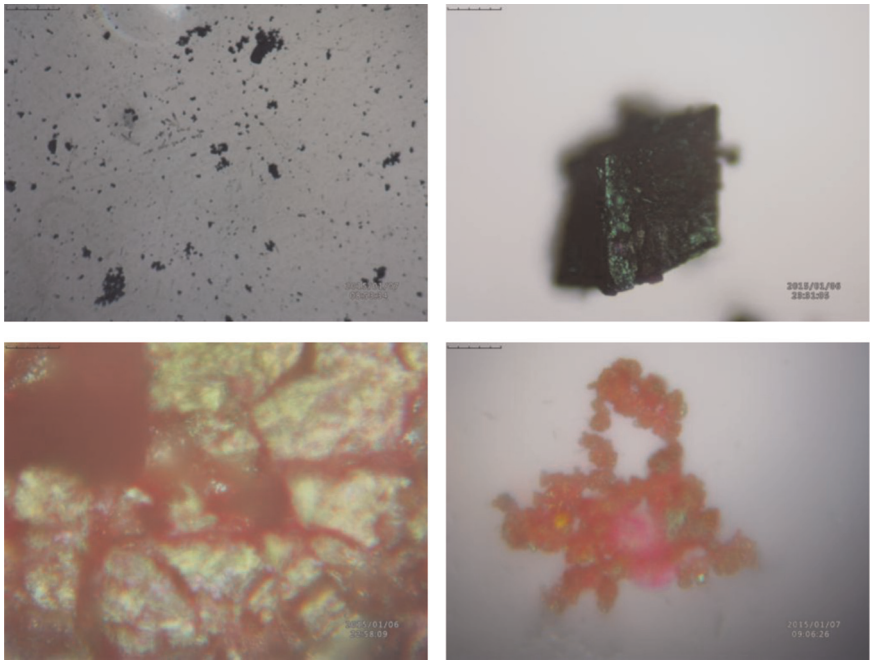

Fig. 2. Optical microscopic images of But-RB solid (scales are shown on the top left of each image, 40 μm/scale for top left image, 8 μm/scale for top right image, and 2 μm/scale for bottom images). Bottom images were taken under excitation light which induces the red fluorescence.