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Nanoscaled rhodamine dyes with 4.5-fold longer fluorescence lifetimes and 150 nm red shifted fluorescence spectra: Preparation, size tuning and optical properties

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ABSTRACT

Nanoscaled rhodamine (NSR) dyes were prepared by reprecipitation method and characterized by TEM and laser diffraction analysis. The optical properties of nano wired rhodamine dyes were studied by UV–vis absorption and steady state/time resolved fluorescence. The size of NSR dyes is tunable by varying the concentration of rhodamine or surfactant additive. Compared to corresponding molecular rhodamine, the fluorescence lifetime of NSR dyes is 4.5-fold longer, while the emission maximum can be 150 nm larger. Although the increase in size of NSR dyes leads to large red shifts in optical absorption and fluorescence spectra, it does not affect the fluorescence quantum yield and lifetime. On the other hand, the presence of a surfactant (sodium dodecyl benzene sulfonate) not only causes the increase in fluorescence quantum yield, but also greatly extends the fluorescence lifetime of NSR dyes from 1.51 ns to 7.07 ns.

1. Introduction

Fluorescent organic nano- and microcrystals have potential applications in modern technologies, such as chemical and biological sensors [1–4] photocatalysts [5], functional materials for optics [6–9] and optoelectronics [10]. In contrast to the extensive studies for semiconductor nano particles, the development of organic nano materials is still a big challenge in science and technology. For example, the preparation of organic particles with precise shape and size is still difficult to control. The optical properties of organic nano particles are still difficult to predict because the correlation with molecular structures, the numerous intermolecular interactions, as well as the particle size and shape, are not yet fully understood [11].

The studies on fluorescent pure organic nanoparticles have been focusing on perylene [12,13], carbazoles [14,15], and cyanine dyes [16,17]. Nanoscaled rhodamine dyes have not been explored in depth on the preparation and properties except for a recent report in which UV-induced formation of rhodamine B nanoparticles was found [18]. On the other hand, rhodamine–inorganic hybrid fluorescent materials, made from incorporation of rhodamine dyes into inorganic nanoparticles, are extensively discussed [19–25]. Rhodamine dyes include several well-known compounds, e. g. Rhodamine B (RB) and its derivatives (Fig. 1), these dyes usually have excellent fluorescence properties and have been widely used in many areas [26].

Based on above considerations, hereby we report the preparation of nanoscaled pure rhodamine particles and their optical properties. It turned out that the nanoscaled rhodamine dyes are one dimensional with diameter in tens of nanometers, while their optical absorption and emission spectra are significantly different from other organic nanoparticles.

2. Experimental section

2.1. Reagents and apparatus

Rhodamine dyes, including Rhodamine B (RB) or C.I. Pigment Violet 1, Rhodamine B ethyl ester (Et-RB), Rhodamine B butyl ester (But-RB), Lissamine Rhodamine (LA-RB), Sulfonyl Rhodamine B

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(Sulfo-RB), were purchased from Beijing Chemical Reagents Ltd. The purity was stated to be better than 97%. Acetone, n-hexane and sodium dodecyl benzene sulfonate (SDBS) were of analytical grade or better and used as received.

2.2. Sample preparation and characterization

But-RB nanoparticle dispersion were prepared by the reprecipitation method, the procedure is similar to that for perylene nanocrystals [27,28]. Rhodamines are well soluble in acetone but not in *n*-hexane which makes reprecipitation method feasible. Typically, the stock solution of But-RB in acetone (2 mmol$\cdot$L^{-1}) was prepared first, then a few micro liters (μL) of this solution was rapidly injected into *n*-hexane (4 mL) at room temperature under ultrasonic processing for 2 min. Particle size control was carried out by: 1) changing the injection volume of the stock solution, 2) adding different amount of surfactant SDBS as a stabilizer to the NSR dispersion.

The preparation procedure of TEM (transmission electron microscopy) samples is as following. One drop of the NSR particle dispersion in n-hexane was taken by pipetting onto a carbon wafer, and dried by natural evaporation before TEM (Hitachi H-7650) observation.

Delsa Nano of Beckman Laulter was used to analyze the particle size by LDPSA (Laser Diffraction Particle Size Analyzing). Typically, a few micro liters (μL) of But-RB acetone solution was rapidly injected into *n*-hexane (3 mL) at room temperature under ultrasonic processing for 2 min. This sample was then immediately used for LDPSA.

2.3. Optical property measurements

The absorption spectra of rhodamies in solution and nanoparticle disperse systems 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 with a 1 cm cuvettes and excitation at 500 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.

Fluorescence quantum yield (Φ_f) was measured by using $\Phi_f = (F_s \cdot A_0 \cdot n_s^2 \cdot \Phi_f^0)/(F_0 \cdot A_s \cdot n_0^2)$, 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 ($\Phi_f^0 = 0.95$) [26].

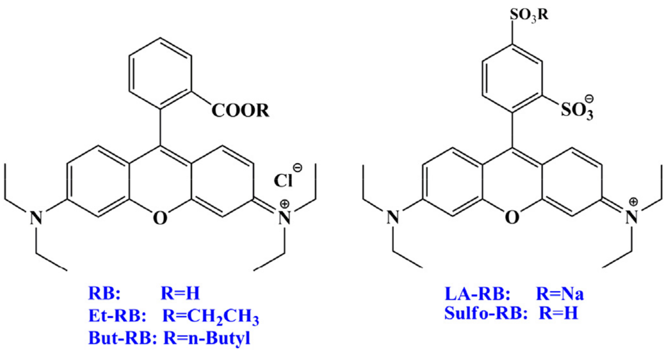

Fig. 1. Chemical structures and abbreviations of rhodamine dyes.

Measurements of fluorescence lifetimes were carried out by standard time-correlated single-photon counting method. The excitation light was a portable diode laser (EPL-375, Edinburgh Instruments), the 379 nm (69 ps, 0.10 mW) 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 both excitation and emission was 2 nm. The prompt response function of the system had an fwhm between 500 and 700 ps. The convolution method was used to obtain the fluorescence lifetime. Time-correlated fluorescence intensity curves (I(t)) were analyzed as multi-exponential decays $I(t) = A + \sum_i B_i \exp(-t/\tau_i)$ in which several fluorescence lifetime τ_i and preexponential factors B_i can be obtained.

3. Results and discussion

Compared to molecular But-RB in solution, the nanoscaled rhodamine shows much longer peak maxima in both optical absorption and fluorescence spectra (Fig. 2). Furthermore, the fluorescence lifetime of the nanoscaled rhodamine is also much longer than that of the molecular rhodamine in solution (Fig. 3). To understand the large change in optical properties of the nanoscaled rhodamine, the size and shape of the nanoscaled rhodamine as well as the associated optical spectra were measured and elucidated as following.

3.1. The size and shape of rhodamine nanoparticles

The rhodamine dyes are all well soluble in acetone, but not soluble in *n*-hexane. This makes it convenient to prepare nano particles using reprecipitation method by injecting the concentrated rhodamine acetone solution into *n*-hexane. Take But-RB as an example. But-RB nanoparticles (NPs) of different sizes were obtained with the procedure which makes us observe the size effect on optical properties possible. NPs of different sizes were made by injecting a different volume of concentrated But-RB solution (1–20 μL, 2 mmol L^{-1}) into *n*-hexane (4 mL). The color of But-RB was changed from red in ACN to purple in n-hexane immediately after the injection, which is due to the formation of NPs. The corresponding UV–vis absorption spectra were shown in Fig. 2. Sonication was maintained during the injection to make the particles uniform in size.

TEM images are shown in Fig. 4, which were obtained from dried NSR on a carbon wafer. The dried samples typically consist of two-headed thin wires with the length in micrometers. However, the diameters of the wires are only 30–45 nm. Please note that the spherical heads are likely formed by the shrinking of wires during drying process via evaporating hexane. In other words, the spherical heads are not likely existent when the wires are still existent in the hexane dispersion.

LDPSA measurement gives the size distribution of NSR prepared from different initial But-RB concentration (Fig. 5). Fig. 5 shows that the dimension of NSR based on LDPSA is also micrometer scaled, coincident with the wire length revealed by TEM. The peak positions in Fig. 5 moves to the right when the concentration is increased. A three-fold increase in the concentration of But-RB led to the size increase from 3 to 6 μm (Fig. 5 bottom right), this change is mainly a reflection of the length of NSR. The average diameter is also increased when one compares the TEM images of NSR in Fig. 4.

3.2. UV–vis absorption spectra

For comparison, the optical properties of molecular rhodamines need to be measured. The rhodamine dyes are all well soluble in