Dyes and Pigments 80 (2009) 212–218

Contents lists available at ScienceDirect

Dyes and Pigments

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

Supramolecular architecture, spectroscopic properties and stability of C.I. Basic Violet 10 (Rhodamine B) at high concentration

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ARTICLE INFO

Article history:
Received 14 April 2008
Received in revised form 30 June 2008
Accepted 1 July 2008
Available online 18 July 2008

Keywords:
Rhodamine B
Self-assembly
Nanocrystals
Stability
Supramolecular architecture
Nanorod

ABSTRACT

The self-assembly behavior, spectroscopic properties and stability of C.I. Basic Violet 10 (Rhodamine B) were investigated at a relatively high concentration. Rod-like dye nanocrystals could be formed by tuning various THF/H_2O volume ratios, leading to increased fluorescence intensity. TEM, zeta-potential measurement and selected-area electron diffraction patterns indicated that the dye nanorods were successfully encapsulated within a silica layer using a sol–gel process. The ensuing silica-coated, dye nanorods exhibited increased fluorescence intensity, non-leachability in polar solvents and high photostability.

1. Introduction

Dyes such as xanthene, cyanine and azo are traditionally used as colorants, as laser materials and as biological probes in many commercial products [1]. Dyes also exhibit diverse optical or electro-optical properties with potential applications in novel devices, e.g., non-linear optical devices [2–5], nano-scale semi-conductor devices [6] and photorefractive applications [7].

It is well known that dye molecules tend to form supramolecular architectures via self-assembly in solution or in adsorbed states [8–15]. For example, Tian et al. [3,16] fabricated low-dimensional nanorods and nanospheres of a stilbazolium-like organic dye with highly monodisperse size using a self-assembly method. They found that the functions of the materials depended on the size and shape. Using dipolar aggregation of merocyanine dyes, Horn and Rieger [4] successfully obtained well-organized helical nanorods. Gesquiere and colleagues [17] prepared disk-like nanoparticles of *N*,*N*′-bis(2,5-di-*tert*-butylphenyl)-3,4,9,10-perylene-dicarboximide of uniform size by a reprecipitation method.

However, due to the weak non-covalent interactions including hydrogen bonds, aromatic π stacking, electrostatic and van der Waal's interactions, the formed supramolecular complexes are usually in equilibrium with their component parts and other undesired complexes. As a consequence, the desired supramolecular architectures have a low yield as well as low stability upon environmental change. To solve this problem, incorporation of dyes into a silica matrix or Si–Ti binary oxide matrix via a sol–gel method is frequently adopted to tailor and stabilize the supramolecular architectures or to exhibit higher fluorescent intensity and higher photostability of C.I. Basic Violet 10 (Rhodamine B; RB) or C.I. Basic Red 1 (Rhodamine 6G; R6G) [18–25]. For example, Avnir et al. [18] embedded R6G molecules in thin silica-glass films and found that undesired aggregation could be avoided because of the cage effect. A red fluorescence shift occurred owing to the rigid cage, and the R6G encapsulated within silica glass also exhibited better photostability. Del Monte and colleagues [19–22] fabricated RB dimers on the porous surface of silica gels and RB nanoparticles by entrapping RB molecules in γ-glycidyloxypropyl trimethoxysilane (GPTMS)-based sol–gel glass. They found that the formation of larger nanoparticles led to fluorescence enhancement. In addition, intercalation of dye molecules into layered inorganic solids could also produce ordered dye molecular aggregates [26–28].

Most of the aforementioned studies were carried out at extremely low concentrations (e.g., 10^{-4} M or even much lower) to avoid undesired aggregates, which would influence the expected electro-optic response. Up to now, very few studies have focused on the aggregation behavior and performance of organic dyes at high concentrations. In the present study, we took RB as an example and investigated the self-assembly behavior, spectroscopic properties

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doi:10.1016/j.dyepig.2008.07.003

and stability of RB dispersions at comparatively high concentration by tuning the volume ratio of tetrahydrofuran (poor solvent) to H_2O (good solvent) to obtain RB nanorod structures at high concentration. To stabilize the formed organic nanostructure, it was further encapsulated within silica using a sol–gel process. The resulting RB product exhibits strong excited fluorescent emission, non-leachability in polar solvents and good photostability.

2. Experimental section

2.1. Materials

Rhodamine B (RB, analytical grade), tetrahydrofuran (THF, analytical grade), tetraethyl orthosilicate (TEOS) and acetic acid (CH_3COOH) were obtained from Sinopharm Group Chemical Reagent Co., Ltd. (China). γ-Glycidyloxypropyl trimethoxysilane (GPTMS) was purchased from Dow Corning. All chemicals were used as received. Double-distilled deionized water was used for preparation of solutions.

2.2. Preparation of RB aggregates

To obtain well-ordered dye architectures, RB was dissolved in a mixture of water (good solvent) and THF (poor solvent) at different volume ratios (THF/H_2O from 1:6 to 6:1). The typical process was carried out as follows: 0.26 g of RB powder was dissolved in 7.8 ml of water by magnetic stirring for 10 min. Then 46.8 ml of THF was injected and stirred for another 150 min, resulting in an RB dispersion of 1×10^{-2} M in 6:1 (v/v) THF/H_2O. Similarly, RB dispersions of the same concentration in 1:6 and 1:1 THF/H_2O were prepared by altering the relative amounts of water and THF. The RB dispersions obtained were denoted as RB-61, RB-11 and RB-16 for THF/H_2O volume ratios of 6:1, 1:1 and 1:6, respectively.

An aqueous RB solution of 1×10^{-2} M was prepared by directly dissolving 0.26 g of RB powder in 55 ml of water. Both the aqueous RB solution and the dispersion of 1×10^{-2} M were diluted to 1×10^{-5} M for comparison purposes.

2.3. Encapsulation of RB aggregates into silica

The RB-61 dispersion was further incubated with a mixture of TEOS (1.8 ml), GPTMS (1.78 ml), THF (1.81 ml) and CH_3COOH (1 ml) for a period of 150 min at room temperature to allow encapsulation in silica. The dispersion obtained was kept at a concentration of 1×10^{-2} M (RB-61Si) and aged in the dark for 24 h before measurements were performed.

2.4. Characterization

UV–vis spectra: absorption spectra were recorded on a UV–vis spectrophotometer (Hitachi UV-3000, Japan) at a temperature of 25 ± 1 °C.

TEM and SAED observations: a transmission electron microscope (TEM; Hitachi H-600, Hitachi, Japan) was used to observe the morphology of RB aggregates. The RB dispersions were dropped onto carbon-coated copper grids and dried at room temperature before examination. Selected-area electron diffraction (SAED) was performed on a JEM 200 CX microscope operated at 160 kV.

SEM observations: a scanning electron microscope (SEM; Philips XL30 apparatus) was used to observe morphological features. One drop of RB dispersion was coated onto aluminum foil and then spun at 5000 rpm for 30 s to produce a film for observation. The film obtained was sputter-coated with gold prior to examination.

pH value: pH value was measured with a digital pH meter (Model PHS-25, Ingold Instrument CO., Ltd., Shanghai, China) at room temperature.

Zeta potential: the zeta potential was measured at 30 runs per analysis using a zeta-potential analyzer (Zetasizer, Model Nano-ZS, Malvern Instrument, UK) at 25 °C.

Leachability measurement: an aliquot of 0.5 ml of aged sol was dip-coated onto cleaned glass (1×1 cm^2) to produce sol–gel thin films. The films were aged and dried in the dark for 7 days. Doped glasses were immersed into four different leaching solvents: H_2O, HCl (0.1 M, pH 1), ethanol and NaOH (0.1 M, pH 13). The absorption spectra and appearance of the leachates were observed to evaluate the leachability.

Emission spectra: the fluorescence emission intensity was measured for all samples with excitation at 560 nm on an FLS 920 spectrophotometer (Edinburgh Instruments, Livingston, UK) immediately after sample preparation.

UV irradiation: photodecomposition was carried out by placing samples in a UV crosslinker with five 8-W UV-C tubes (wavelength 365 nm, 3.1 mW/cm^2, Model XLE-1000, Spectroline, USA). After UV irradiation, the emission intensity was measured as a function of the UV irradiation time. The ratio of I_t/I_0 was adopted to evaluate the photostability of RB, where I_t denotes the height of emission

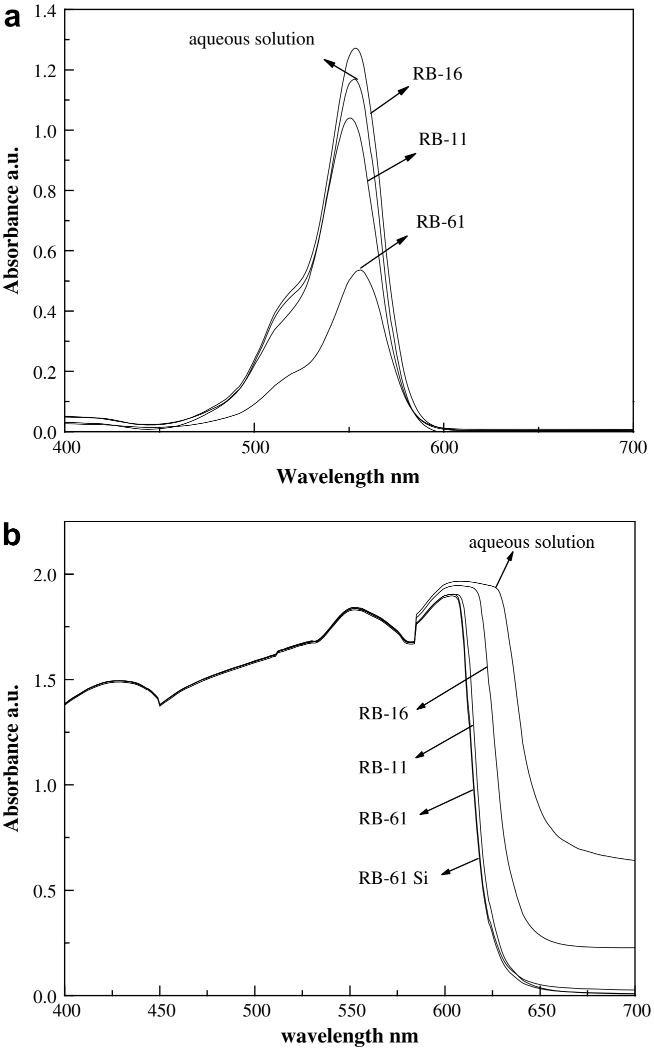

Fig. 1. Effect of THF/H_2O ratios on the absorption spectra of RB solutions and dispersions. (a) 1×10^{-5} M, and (b) 1×10^{-2} M (cell length: 1 mm).