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Enhancement of fluorescence from one- and two-photon absorption of hemicyanine dyes by confinement in silicalite-1 nanochannels

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ABSTRACT

We prepared unique organic–inorganic composite possessing strong one- and two-photon florescence properties by encapsulating hemicyanine molecules in nanosized silicalite-1 zeolite. The free hemicyanine dye in solvent and confined hemicyanine dye in nanochannels of silicalite-1 showed identical optical one- and two-photon absorption coefficients. By contrast, the fluorescence quantum yields of confined hemicyanine molecules in silicalite-1 channels from one and two-photon absorption were 5- and 3.3-fold, respectively, higher than those of free hemicyanine solution. Such contrasting behaviors in fluorescence were attributed to the isolation and confinement of hemicyanine in nanochannels of silicalite-1. This study represents a promising new strategy in the development of one- and two-photon fluorescence materials and a novel direction for zeolite research and its application in the development of optical materials.

1. Introduction

To date, considerable research attention has been focused on developing novel photoluminescence materials having unique luminescent properties based on organic–inorganic composites [1–22]. Traditionally, inorganic nanopore-structured materials, such as zeolite [3–17]; metal-organic frameworks [18–20]; and clay [21,22] have been utilized to produce inorganic and organic photoluminescent materials. Zeolite and related porous materials have been extensively developed into versatile inorganic hosts to prepare practically viable organic–inorganic composites for photoluminescence materials [3–6], nonlinear optical (NLO) materials [7–12], micro-laser [13] and energy transfer materials [14–17] because of their ability to confine guest molecules in their rigid nanopore structures. Among the various types of zeolites, the MFI-type structures such as ZSM-5 and silicalite-1 (SL-1), a centrosymmetric (Pnma space group) zeolite with a three-dimensional channel system comprising straight 0.54 × 0.56 nm^2 channels in one direction and sinusoidal 0.51 × 0.54 nm^2 channels perpendicular to the straight channels (as illustrated in Scheme 1), have been used to incorporate dipolar nonlinear organic dyes into their nanochannels and applied in NLO materials [11,12].

Two-photon excited emission from two-photon absorption (denoted as 2PA) materials is extremely important because of its practical application in areas such as optical storage [23,24], biological imaging [25,26], and photodynamic therapy [27,28]. There is great demand for the design of applicable materials with high 2PA cross-section coefficients and emission properties. Particularly for biophotonic applications, it is necessary that 2PA materials are water soluble or dispersible and remain highly fluorescent in aqueous media [29]. However, designed 2PA fluorescent molecules are generally hydrophobic. And their fluorescence quantum yield (denoted as QY) are significantly reduced in aqueous solution because of molecular aggregation, which leads to fluorescence quenching. Consequently, a new design for 2PA materials is required to improve 2PA activity and enhance the emission QY of 2PA processes [30,31].

Several methods have been recently reported for enhancing light emission upon aggregation or in the solid state; these techniques involve the restriction of intermolecular vibration and rotation. Such approaches offer a novel way to address aggregation-caused quenching [31,32]. However, problems such as solubility, stability, and control of concentration for real applications in aqueous media must still be overcome.

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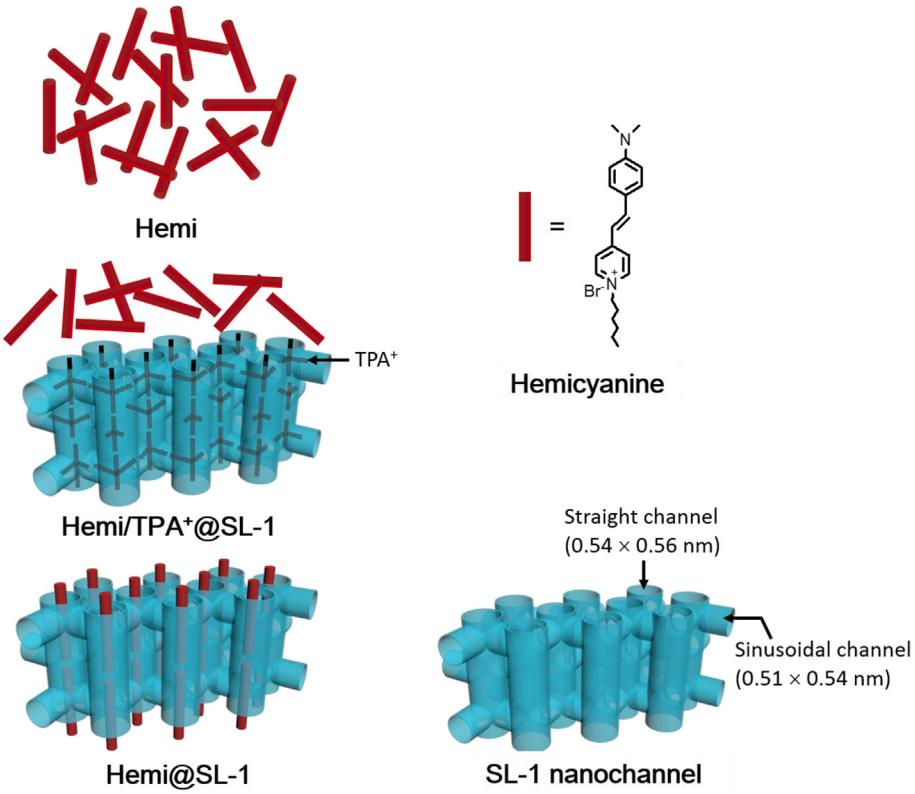

Scheme 1. Schematic illustrations for Hemi, Hemi/TPA$^+$@SL-1, and Hemi@SL-1, respectively, with hemicyanine molecule and SL-1 nanochannel structural.

The utilization of zeolites as host materials that stabilize and confine guest molecules in nanochannels could be an excellent solution to the above mentioned problems. For example, zeolites and related nanoporous materials have been intensively investigated as hosts for the aligned inclusion of organic dipolar NLO dyes to develop novel organic–inorganic composite NLO materials. As a result, the potential of zeolites and related nanoporous materials as versatile inorganic hosts for preparing of practically viable organic–inorganic composite second-harmonic generation materials has been demonstrated [11,12].

Herein, we report the preparation of a fully dispersible nanosized SL-1 powder that was used to confine hemicyanine, which has a large 2PA cross section in its nanochannels. We evaluated the one photon absorption (denoted as 1PA) and 2PA and emission properties of nanochannel-confined hemicyanine, and then compared them with those of freely solvated hemicyanine in solution. Furthermore, the effect of environment on the 1- and 2PA optical emission of the material was investigated.

2. Experimental section

2.1. Preparation of nanosized SL-1 powder

A gel consisting of tetrapropylammonium hydroxide (TPAOH), tetraethyl orthosilicate (TEOS), NaOH, and H_2O was prepared by weighing TPAOH (18 g), TEOS (10.4 g), NaOH (12.8 mg), and distilled deionized water (DDW, 18 mL) into a 100 mL plastic beaker and stirring vigorously for 90 min at room temperature. After the gel solution became clear, it was transferred to a 100 mL round bottom flask and heated at 60 °C for 146 h with continuous stirring. The SL-1 was then collected by centrifugation (20 min, 9000 rpm, room temperature) and washed five times with an ethanol/DDW mixture (3:5, v/v) before being oven dried at 60 °C overnight and calcined at 550 °C for 12 h.

2.2. Inclusion of hemicyanine dye into SL-1

Hemicyanine-6 solutions (HC-6, 1.0 mM) in two different solvents were obtained by dissolving HC-6 (7.8 mg) in dimethyl sulfoxide (DMSO, 20 mL) or DDW (20 mL). Each solution was diluted five times with DMSO or DDW, respectively, to afford 200 μM solutions. SL-1 (30 mg) was then added to 10 mL of each HC-6 solution in a 15 mL conical tube.

2.3. Characterization of optical properties

For one photon absorption spectra, UV–vis spectra were taken with a Shimadzu UV-2600. And fluorescence spectra from one photon excitation were obtained from Jasco FP-6300.

The schematic layout of the 2PA and two-photon excitation fluorescence (denoted as 2PF) measurement setup is shown in Fig. S1. The 2PA spectra were measured through 2PF described by Bhaskar et al. [33]. A femtosecond Ti: sapphire oscillator and amplifier system (Coherent) was used to pump an optical parametric amplifier (OPA, Coherent TOPAS) as the excitation source (pulse duration, 50 fs; repetition rate, 1 kHz; and pulse energy, 500 nJ). The OPA output pulse with the range of 800–1100 nm (~100 mW average power) was generated by second harmonic generation and used to induce 2PA-induced fluorescence as excitation source. The incident beam with the desired wavelength was focused using a convex lens (focal length = 20 cm) and directed to a 1 mm cuvette containing sample. The sample was tilted at 45° along the on-axis of the focused beam. The fluorescence signal collected at 135° from the sample was sent through a mirror and convex lens (focal length = 20 cm), dispersed by a monochromator