Changes in Fluorescence, Color, and Morphology of Fluorescent Nanostructures under Successive Light Irradiation

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Fluorescence, color, and morphological changes of fluorescent nanostructures consisting of azobenzene-containing chromophores were investigated under successive visible light irradiation. Compared with spheres composed of a chromophore showing sufficient photoisomerization, fluorescent nanofibers assembled from a molecule showing a very small amount of photoisomerization had a slow response to light. Successive visible light irradiation of the nanofibers led to changes in fluorescence intensity and color, whereas the one-dimensional morphology was hardly affected. UV-visible absorption spectroscopy, optical microscopy (OM), scanning electron microscopy (SEM), and fluorescence optical microscopy (FOM) were employed to confirm the light-responsive properties. Our observations suggest that sufficient photoisomerization plays a key role in realizing fast and efficient light response of self-assembled structures.

Keywords: Color, Fluorescent Nanostructure, Light, Morphology

1. Introduction

Stimuli-responsive fluorescent materials have received considerable attention owing to their fundamental researches and practical applications in sensors, actuators, display, and memory devices [1-5]. To alter the morphology and fluorescence property of self-assembled nanostructures, supramolecular systems are formed through noncovalent interactions including π - π stacking, van der Waals, hydrophobic effects, electrostatic interactions, and so on [6-11]. Fluorescent organic materials that respond to external stimuli such as light, temperature, mechanical forces and chemicals have been developed [1-7,12]. Compared with other stimuli, light acts as a useful trigger because it is possible to tune its wavelength and intensity a non-contact and remote-controlled manner.

Han *et al.* designed a new type of trigonal azobenzene-containing chromophore (3BrAz and 3BuAz, see Scheme 1) with aggregation-induced emission/aggregation-induced

enhancement (AIE/AIEE) property [3,4]. 3BuAz underwent sufficient photoisomerization (~90%) and the self-assembled spheres exhibited significant light-driven morphological changes and the resulting decreases in fluorescence intensity [13]. However, although red fluorescence from 3BrAz nanofibers was reduced by external stimuli such as pressure, friction, and thermal treatment owing to decreases in the degree of crystallinity [14], the light-responsiveness has not been explored yet on the basis of the light-induced molecular structure

Scheme 1.

change. Here, we investigated the photoisomerization behavior of 3BrAz in dilute solution and the light response of 3BrAz nanofibers. In contrast to 3BuAz, the molecular structure of 3BrAz was rarely changed by light even in solution. Changes in fluorescence, color and morphology of the 3BrAz nanofibers by successive light irradiation were monitored using optical microscopy (OM), fluorescence optical microscopy (FOM), and scanning electron microscopy (SEM) experiments.

2. Experimental

Spectroscopic-grade tetrahydrofuran (THF) solvent was used to dissolve 3BrAz and 3BuAz. Each azobenzene solution was placed in a clean quartz cell and sealed with parafilm after 30 seconds nitrogen purging. The absorption and fluorescence spectra were taken after 30 and 40 min of sample preparation, respectively.

To produce self-assembled structures, we added water dropwise to the 3BrAz in THF solution with gentle shaking. As the water content increased, the mixture solution started turning turbid and a floating suspension was produced. Largely entangled fiber wads separated slowly from the solvent mixture. OM, FOM and SEM samples were then prepared by placing one drop of the red entangled fiber wad on a clean glass substrate and allowing it to fully dry at room temperature.

UV-vis absorption and fluorescence spectra were obtained using a Shimadzu UV-2600 UV-vis spectrophotometer and a Horiba FluoroMax-4 spectrofluorometer, respectively. The SEM samples were first coated with a platinum layer for 60 seconds using a Hitachi E-1030 ion sputter. The SEM images were recorded by using a TESKAN-MIRA3-LM microscope. The optical microscopy and fluorescence optical microscopy images were obtained using an Olympus BX53 microscope equipped with an Olympus WIG fluorescence cube ($\lambda_{\text{ex}} = 520\text{--}550\text{ nm}$).

3. Results and discussion

UV-visible absorption spectroscopy was used to monitor the light-induced molecular structure change of 3BrAz in dilute THF solution. The absorption spectrum of freshly prepared 3BrAz solution displayed two strong absorption bands centered at 362 and 478 nm, and red-shifted absorption bands were recorded in the 3BuAz spectrum (Fig. 1a). 3BrAz and 3BuAz solutions showed very weak fluorescence centered at around 570 and 610 nm, respectively (Fig. 1b). Figure 1c

Fig. 1. (a) UV-vis absorption spectra of 3BrAz and 3BuAz in THF. (b) Fluorescence spectra of 3BrAz and 3BuAz in THF ($\lambda_{\text{ex}} = 510\text{ nm}$). (c) Absorption spectral changes of 3BrAz in THF as a function of exposure time of UV light at 365 nm. (d) Absorption spectra before (solid line) and after (dashed line) the formation of 3BrAz fibers.

shows UV-visible absorption spectral changes of 3BrAz solution as a function of exposure time of UV light at 365 nm. Even after irradiation with UV light for 10 min, two characteristic absorption bands were changed by only <4%. That is, light irradiation scarcely seemed to generate an isomer with a sufficient lifetime [15,16]. This is in sharp contrast to 3BuAz which showed ~90% of light-induced molecular structure changes and slow thermal back isomerization [13].

Self-assembled structures were formed using a simple reprecipitation method. As water was added into 3BrAz THF solution, the mixture solution started turning turbid due to the occurrence of self-assembled aggregates. Subsequently, largely entangled 3BrAz fiber wads slowly sank to the bottom of the quartz cell. Upon the formation of fibers, two characteristic absorption bands were red-shifted and a shoulder band at around 560 nm appeared (Fig. 1d). These spectral changes would be associated with inclined molecular arrangements of the chromophores in the fibers (*i.e.*, J-aggregation).

OM and SEM measurements revealed that reddish-brown 3BrAz fibers were <100 nm wide and over tens of micrometers long (Figs. 2a and 3b). This observation is in agreement with the previous study [14]. The narrow nanofibers tended to

Fig. 2 (a) OM, SEM (inset), and (b) FOM ($\lambda_{\text{ex}} = 520\text{--}550\text{ nm}$) images of 3BrAz nanofibers prepared from $5 \times 10^{-5}\text{ M}$ THF/ H_2O (1:4, v/v). (c) FOM image of nanofibers taken after irradiation with green light for 6 min. (d) FOM and (e) OM images taken after irradiation with green light for 60 min. The white inset line profiles in (b, c, d) indicate changes in the relative fluorescence intensities corresponding to the white arrow lines.

agglomerate together to generate macroscale fiber wads. As clearly seen in the FOM image (Fig. 2b), compared with isolated nanofibers, highly entangled fiber wads displayed stronger red fluorescence, confirming AIE/AIEE characteristics. On the other hand, these dried fibrous structures did not show fluorescence when excited with UV or blue light from a mercury lamp.

We next investigated the light-responsiveness of 3BrAz nanostructures. The inset profiles in Fig. 2b–2d exhibit the variations in the relative fluorescence intensities corresponding to the white lines in the FOM images. The fluorescence intensity of 3BrAz

nanofiber was reduced by approximately 40% after irradiation with light for 6 min (Figs. 2c and 3a). Additional irradiation with green light for 10 min led to significant decreases in the red fluorescence intensity, and consequently the fluorescence almost disappeared (Fig. 2d). The OM image taken after green light irradiation for 60 min demonstrates that the relatively isolated red fibers turned orange-brown, while the largely entangled fiber wads retained their original brown color (Fig. 2e). Such slow decoloration and fluorescence decrease seems to be caused not by light-induced isomerization of 3BrAz, but by prolonged light irradiation.

To obtain more information about the morphological changes during green light irradiation, we conducted SEM measurements. Compared with the as-prepared fibrous structures (Fig. 3b), the largely entangled fibers kept their one-dimensional shapes almost intact even after green light irradiation for 60 min (Fig. 3c). But, the relatively isolated fibers looked somewhat flat. The slight morphological changes seem to be associated with the prolonged light irradiation which might disturb fast thermal back isomerization and might raise the temperature of the sample to some extent.

For comparison, red fluorescence from 3BuAz spheres decreased drastically after irradiation with green light for 1–2 min and fully vanished after irradiation for 4 min (Figs. 3a and 4). The resulting liquefaction of spherical objects was observed clearly. As a consequence, the relatively fast light response is attributed to fast and sufficient photoisomerization of 3BuAz molecule and slow thermal back isomerization [17,18].

Fig. 3. (a) Changes in relative fluorescence intensities of 3BrAz nanofibers and 3BuAz spheres as a function of green light irradiation time. SEM images of 3BrAz nanofibers (b) before and (c) after exposure to green light for 60 min.

4. Conclusion

We have presented light-induced fluorescence, color and morphological changes in fluorescent self-assembled aggregates composed of

Fig. 4. (a) OM, SEM (inset) and (b) FOM images of 3BuAz spheres. (c) FOM image taken after irradiation with green light for 2 min. The inset line profiles in (b and c) indicate changes in the relative fluorescence intensities corresponding to the white arrow lines.

azobenzene-containing chromophores. Successive visible light irradiation of nanofibers generated from 3BrAz chromophore showing a very small amount of photoisomerization resulted in slow decoloration and fluorescence decrease, but the morphology was hardly affected by light. These results support that light-induced morphological changes seem to be mainly derived from large changes in the molecular structure of the constituent molecules. Our investigations suggest that an important key to realizing fast and efficient light response depends on molecular design strategies for photochromic compounds showing sufficient photoisomerization.

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