Mechanochromic Luminescence Exhibited by Supramolecular Fibers Consisting of Dumbbell-shaped, Hydrophobic Molecules

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Abstract

A variety of mechanochromic fluorescence materials based on change in molecular assembly have been reported so far. When used as practical mechano-sensors, low-dimensional molecular assemblies are preferable. In this study, mechanochromic supramolecular fibers consisting of a dumbbell-shaped hydrophobic molecule were developed to expand the range of potential applications. Solid samples of these supramolecular fibers changed the fluorescence color from green to yellow by grinding. Upon subsequent thermal treatment, the fluorescence color changed from yellow to green.

1. Introduction

Mechanochromic luminescence materials, which change the photoluminescence properties in response to mechanical stimuli, have been investigated because such mechano-sensing materials visualize the damaged part of the materials.[1,2)] When used as practical mechano-sensors, low-dimensional molecular assemblies are preferable. Based on this consideration, water-soluble mechanochromic fluorescence micelles[3)] and hydrophilic supramolecular fibers[4)] that become water-soluble upon grinding have been developed. Here, we report mechanochromic fluorescence supramolecular fibers consisting of highly hydrophobic molecules in order to expand the range of the potential applications of such materials.

2. Results and discussion

The molecular structure of 9,10-bis(phenylethynyl)anthracene derivative **1** is shown in Fig. 1. Two hydrophobic dendritic structures were introduced into the fluorophore through amide groups. To increase solubility in hydrophobic solvents, eight dodecyloxy groups were introduced at the peripheral position of the dendrons.

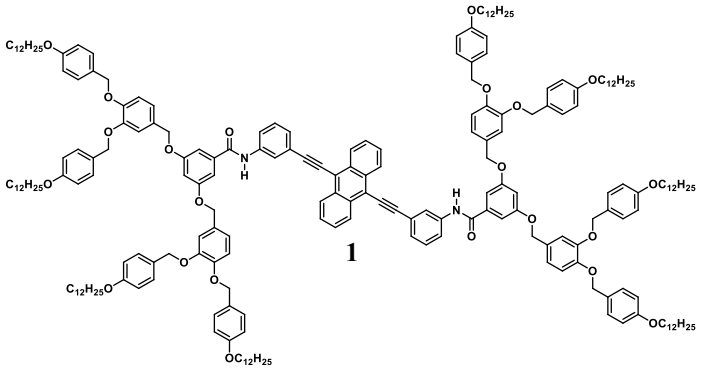

Fig. 1. Molecular structure of dumbbell-shaped hydrophobic compound **1**.

First, the absorption and fluorescence properties of **1** in solutions were examined (Fig. 2).

Compound **1** in dichloromethane (DCM) was in the monomeric state, while redshifts were observed in both the absorption and the fluorescence spectra in the mixture of DCM and methylcyclohexane (MCH) (1:9 v/v), suggesting that the fluorophores formed *J*-aggregate arrangements.

Next, atomic force microscopy (AFM) observation was conducted to investigate supramolecular assemblies of compound **1** in the DCM/MCH solution. Samples were prepared by spin-coating the solution onto a highly oriented pyrolytic graphite (HOPG) substrate. As shown in Fig. 3, compound **1** formed supramolecular fibers with a height of ca. 1.5 nm on the HOPG substrate.

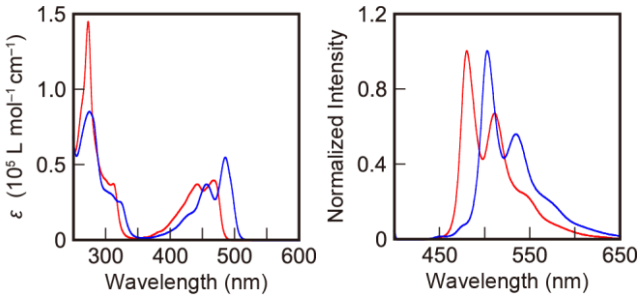

Fig. 2. Absorption (left) and fluorescence (right) spectra of compound **1** in DCM (red line) and DCM/MCH (1:9 v/v, blue line). $c = 1.0 \times 10^{-5}$ M. $\lambda_{ex} = 400$ nm.

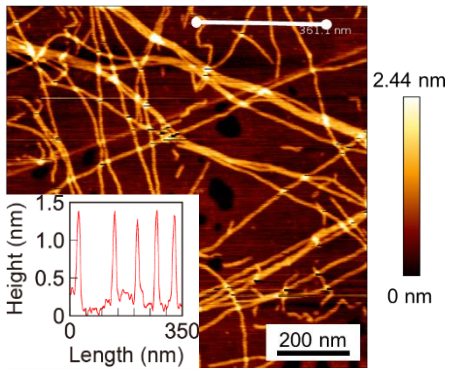

Fig. 3. An AFM image of supramolecular fibers consisting of **1**. The inset shows the height profiles of the supramolecular fibers.

External stimuli-responsive luminescence of the supramolecular fibers was investigated. A solid sample of the supramolecular fibers was obtained after vacuum drying compound **1** in the DCM/MCH solution. The sample of compound **1** displays monomer-like photophysical properties in the initial solid state (Fig. 4). When this solid was ground, the fluorescence color changed from green to yellow, resulting from excimer formation. Moreover, when the ground sample was heated at 120°C for 10 minutes, the fluorescence color changed from yellow to green. This suggested that the excimer formations are not retained.

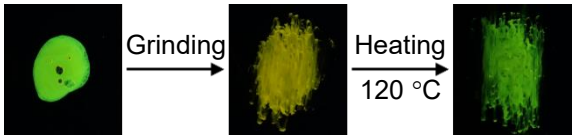

Fig. 4. External stimuli-responsive luminescent color changes of **1**. $\lambda_{ex} = 365$ nm.

3. Conclusions

In this study, we developed mechanochromic supramolecular fibers consisting of the dumbbell-shaped hydrophobic molecule **1**. This molecule was in the monomeric state in DCM, while it formed supramolecular fibers in the highly hydrophobic solvent mixture of DCM/MCH. Solid samples of these supramolecular fibers exhibited a change of fluorescence color from green to yellow by grinding. Upon subsequent thermal treatment, the fluorescence color changed from yellow to green.

References

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