

Article

Photomechanical Bending of Azobenzene-Based Photochromic Molecular Fibers

Hideyuki Nakano *, Ryoji Ichikawa and Riku Matsui

Department of Applied Chemistry, Muroran Institute of Technology, 27-1, Mizumoto-cho, Muroran, Hokkaido 050-8585, Japan; E-Mails: s2027006@mmm.muroran-it.ac.jp (R.I.); s2123203@mmm.muroran-it.ac.jp (R.M.)

* Author to whom correspondence should be addressed; E-Mail: nakano@mmm.muroran-it.ac.jp; Tel.: +81-143-46-5753; Fax: +81-143-46-5701.

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Abstract: Microfibers composed of azobenzene-based photochromic amorphous molecular materials, namely low molecular-mass photochromic materials with a glass-forming property, could be fabricated. These fibers were found to exhibit mechanical bending motion upon irradiation with a laser beam. In addition, the bending direction could be controlled by altering the polarization direction of the irradiated light without changing the position of the light source or the wavelength of the light. *In-situ* fluorescence observation of mass transport induced at the surface of the fiber doped with CdSe quantum dots suggested that the bending motions were related with the photoinduced mass transport taking place near the irradiated surface of the fiber.

Keywords: photomechanical effect; photochromic molecular fiber; azobenzene; photoinduced mass transport; bending motion; CdSe quantum dot

1. Introduction

Since photo-controllable motors and actuators are expected to provide prospective wireless and electrodeless micromachine systems, creation of new photomechanical materials, elucidation of the mechanism of their photomechanical motions, and their application to photo-controllable micromachines are subjects of interest. Photomechanical motions due to the photothermal effect of conventional polymers doped with dyes were investigated in the 1990s and shown to be applicable to

all-optical devices [1,2]. Recently, photomechanical effects observed for photochromic materials due to reversible photochemical reactions have been attracted a great deal of attention. For example, photomechanical bending motions of a variety of azobenzene-based polymers and azo-dye doped polymer systems which related the trans-cis photochromic reactions of azo-moiety have been reported [3–11]. With regard to materials composed of low molecular-mass compounds, needle- and plate-shaped microcrystals of diarylethene, anthrathene, and azobenzene derivatives have been reported to exhibit reversible bending motions by photoirradiation [12–14]. Such reversible mechanical motions of photochromic materials in bulk scale are believed to be caused by cooperation of the motions in molecular levels upon photoirradiation. The bending directions of such materials were suggested to depend on the kinds of molecules and their alignments in these materials; therefore, it is difficult to change the bending direction without changing the position of the light source and the wavelength of the light.

We have been performing studies of the creation of a low molecular-mass photochromic compound which readily form amorphous glasses, namely “photochromic amorphous molecular materials” [15–19]. Among these, azobenzene-based photochromic amorphous molecular materials were found to exhibit trans-cis photo-isomerization reactions as amorphous films as well as in solutions [15,18]. In addition, several photomechanical effects of azobenzene-based photochromic amorphous molecular materials and crystalline materials caused by photoinduced mass transport have been found [20–29]. In our previous communication [27], we have reported that the photomechanical bending motions of a microfiber composed of an azobenzene-based photochromic molecular materials, which we refer to as “photochromic molecular fiber”, using 4-bis[(9,9-dimethylfluorenyl)amino]azobenzene (BFIAB), and that the bending direction of the fiber could be controlled by altering the polarization direction of the irradiated light. After that, photomechanical bending motions depending upon polarization directions of incident light were reported for azobenzene-functionalized polyimides [30,31].

In the present study, we have fabricate molecular fibers composed of other azobenzene-based photochromic amorphous molecular materials, 4-bis[4-(methylphenyl)amino]azobenzene (BMAB), 4-di(biphenyl-4-yl)aminoazobenzene (DBAB), and 4-bis[(9,9-dimethylfluorenyl)amino]-4'-nitroazobenzene (NO₂-BFIAB), and investigated their photomechanical bending motions. In addition, photoinduced mass transport taking place at the irradiated surface of the fiber was observed *in-situ* using BFIAB molecular fiber doped with CdSe quantum dots (QDs).

Figure 1. Chemical structures of the materials used in the present study. (a) BFIAB; (b) BMAB; (c) DBAB; (d) NO₂-BFIAB.

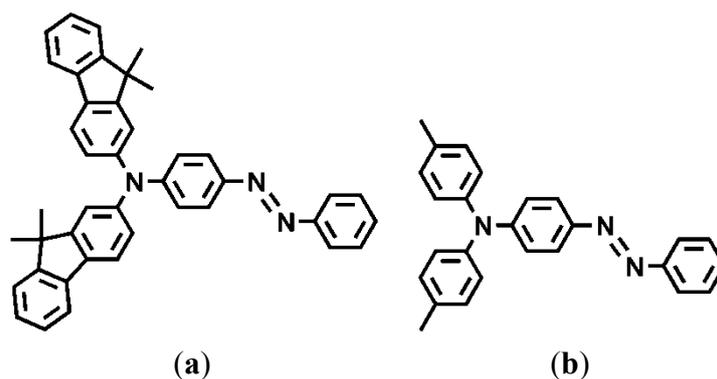
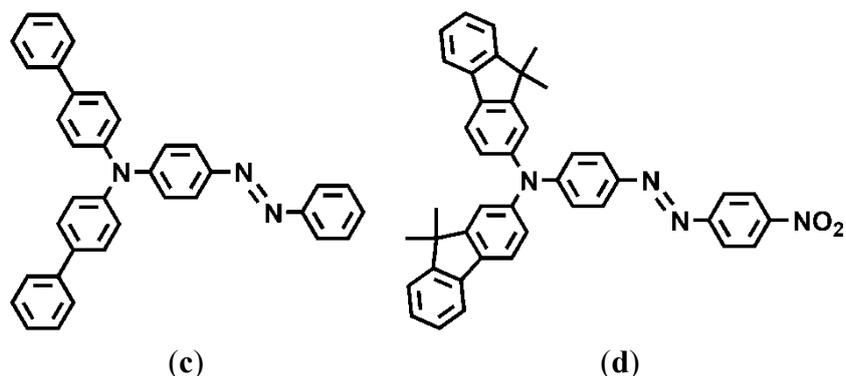


Figure 1. Cont.



2. Experimental Section

2.1. Materials

BMAB, DBAB, BFIAB, and NO₂-BFIAB were prepared according to our previous papers [18,24]. Glass transition temperatures (T_g) of BMAB, DBAB, BFIAB, and NO₂-BFIAB were 27 °C, 68 °C, 97 °C, and 117 °C, respectively. CdSe-based QDs dispersed in toluene was purchased commercially (Core Shell EviDots™, ED-C11-TOL-0620, EM: 612 nm, Evident Technologies Inc., New York, NY, USA).

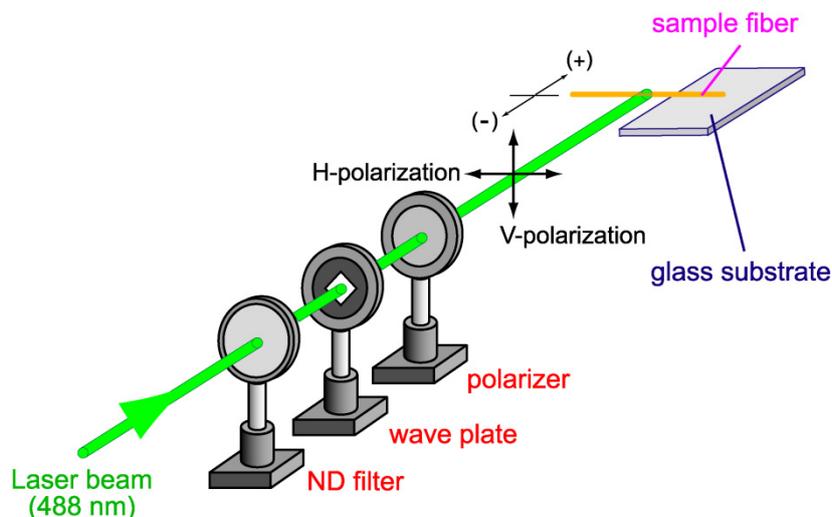
2.2. Preparation of Molecular Fibers

The powder of BMAB, DBAB, BFIAB, or NO₂-BFIAB was heated above the melting point on a glass substrate. After that, the molten sample was slightly cooled and kept at the appropriate temperature just under the melting point. A part of the resulting viscous supercooled liquid sample was anchored with a pair of tweezers and then drew it up to readily form a fiber.

In order to prepare the BFIAB fiber doped with QDs, appropriate amount of BFIAB was dissolved in the QDs-dispersed toluene solution and a few drops of the solution put on a heated glass substrate at *ca.* 120 °C, resulting in evaporation of the solvent. Using the resulting mixture of BFIAB and QDs, a fiber was fabricated by the same procedure as a method to fabricate molecular fibers described above.

2.3. Optical Microscopy

The sample fiber was irradiated with a linearly polarized laser beam (488 nm, CYAN-488-100 CDRH, SpectraPhysics Inc., Cambridge, UK) with a polarization direction either parallel (H-polarized light) or perpendicular (V-polarized light) to the fiber axis and with an intensity of *ca.* 400 mWcm⁻² through a ND filter, a wave plate and a polarizer at room temperature (*ca.* 20 °C) as shown in Figure 2. Bending behavior of the fiber was monitored using a Stereoscopic Microscope (Nikon) attached with a CCD camera (VB-7010, Keyence, Osaka, Japan) through a cut-off filter (Y-51, AGC Techno Glass Co. Ltd, Shizuoka, Japan). Emission of QDs doped in the fiber upon irradiation with the laser beam was observed by means of a microscope (Optiphot X2, Nikon, Tokyo, Japan) through a cut-off filter (<520 nm).

Figure 2. Schematic experimental set-up for photoirradiation of the molecular fibers.

3. Results and Discussion

3.1. Photoinduced Bending Motions of Molecular Fibers

As well as a photochromic molecular fiber of BF1AB [27], molecular fibers of BMAB, DBAB, and NO₂-BF1AB could be fabricated by drawing the molten samples at the temperatures just below their melting points, similar to the melt spinning method used in the fabrication of polymer fibers. Although the accurate control of the diameter of the fiber was difficult at present due to hand working, molecular fibers with diameters of *ca.* 10–200 μm could be easily obtained. Using these fibers with a diameter of *ca.* 15 μm and with a proper length, behaviors of the fibers upon irradiation was investigated. Schematic experimental set-up was shown in Figure 2.

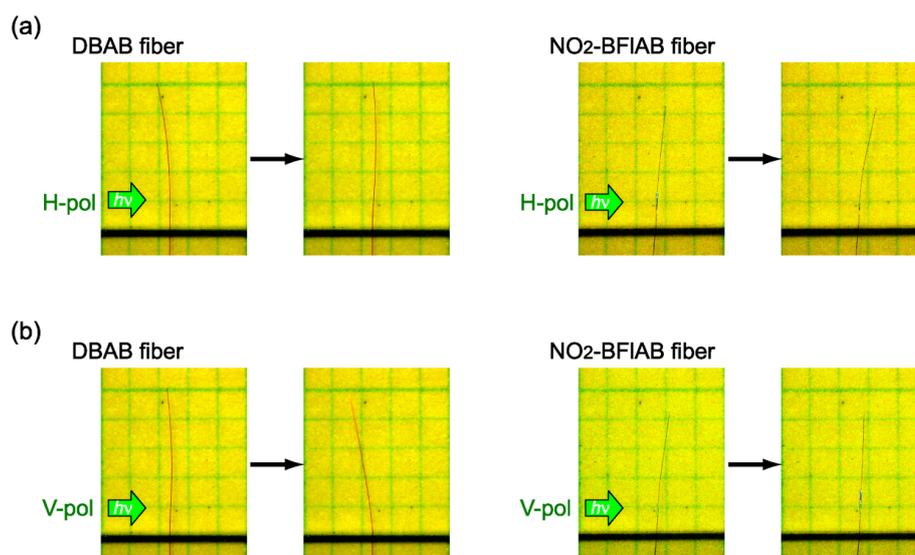
Whereas the BMAB fiber fell down upon irradiation with the laser beam, the fibers of DBAB and NO₂-BF1AB exhibited photomechanical bending motions without falling down as described below. It is conceivable that the temperature of the irradiated area was somewhat raised. At the same time, the material softened due to trans-cis and cis-trans isomerization reactions induced by photoirradiation. Thus, it was suggested that relatively low T_g (27 °C) causes the falling down of the BMAB fiber upon irradiation and that the temperature of the irradiated area of DBAB, and NO₂-BF1AB was low enough compared to their T_gs.

The photomechanical motions of DBAB and NO₂-BF1AB fibers were also investigated. Here, the bending directions of the fiber opposite and toward the light source were defined as positive and negative directions, respectively, as shown in Figure 2.

When the DBAB and NO₂-BF1AB fibers were irradiated with an H-polarized laser beam, the fibers bent slightly in the positive direction at initial stage, perhaps due to volume expansion caused by increase in temperature at the irradiated surface. Upon continuous irradiation, further bending in the positive direction gradually took place as shown in Figure 3a. When the V-polarized light was used, initial bending motion in the positive direction due to photo-thermal effect was observed, similar to that observed when the H-polarized light was used. However, the subsequent continuous irradiation for a longer period induced the mechanical motion in the negative direction as shown in Figure 3b. In

addition, the reverse motion in the positive direction for the resulting fiber could be induced by irradiation with the H-polarized light. Likewise, the reverse motion in the negative direction for the fiber bent in the positive direction by irradiation with the H-polarized light could be induced by irradiation with the V-polarized light. Thus, the fibers could be bent in both directions easily by just altering the polarization direction of the irradiated light without changing the position of the light source and the wavelength of the light. These results were quite similar to that observed for BFIAB fiber [27]. Therefore, such photomechanical motions were suggested to be general phenomena for photochromic molecular fibers. It is notable that such photomechanical motions could not be observed for the fibers with relatively thick diameters ($>ca.$ 30 μm). From the extinction coefficient of the present materials [18,25], penetration depth of the incident laser beam into the fiber was estimated to be $ca.$ 100–200 nm, considerably smaller than the diameter of the fiber. These facts suggested that the present photomechanical motions were related with the phenomena taking place at the irradiated surface of the fiber.

Figure 3. Photomechanical bending motions of DBAB and NO₂-BFIAB molecular fibers upon irradiation with (a) H-polarized laser beam (b) V-polarized one. Interval of grid lines: 1 mm.



3.2. Photoinduced Mass Transport at Irradiated Surface of the Fibers

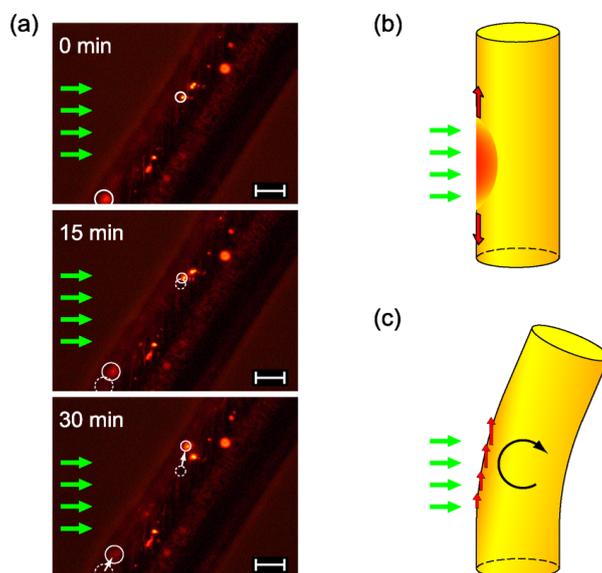
The mechanism of the photomechanical bending of fibers of azo-dye doped polymer and azobenzene-based nematic liquid crystalline polymers have been proposed, which related the change in orientation of the azo-moiety to align perpendicular to the polarization direction of the incident light and/or photothermal effect [5,10,11]. Photomechanical response of azobenzene-functionalized polyimide was interpreted by the traction of the material existing at the irradiated area due to trans-cis isomerization of azo-moiety aligned parallel to the polarization direction of the incident light [3,5,30,31]. We have, however, reported that the molecular fiber of BFIAB was in amorphous state [27] and that dichroism of the material was scarcely able to be induced by irradiation with linearly polarized light [32]. In addition, the bending directions upon H- and V-polarized lights observed in the present study were opposite to those reported to azobenzene-functionalized polyimides [30,31]. Thus, the present photomechanical bending motions of molecular fibers depending

upon the polarization directions of the incident laser beams were considered to be due to the different mechanism.

We have reported that the photoinduced mass flow could be induced at surface level of amorphous films of azobenzene-based photochromic amorphous molecular materials upon angled irradiation using a p-polarized laser beam [29]. Therefore, mass transport was suggested to be induced at surface level of the present molecular fibers upon irradiation, resulting in photomechanical bending motions. In the present study, mass transport induced near the irradiated surface of the fiber was investigated *in situ* by monitoring fluorescence emission of QDs doped in the BF1AB fiber. Here we used the QDs-doped BF1AB fiber with thicker diameter than 50 μm and with both ends fixed in order to avoid the fiber escaping from the microscope field by photomechanical bending.

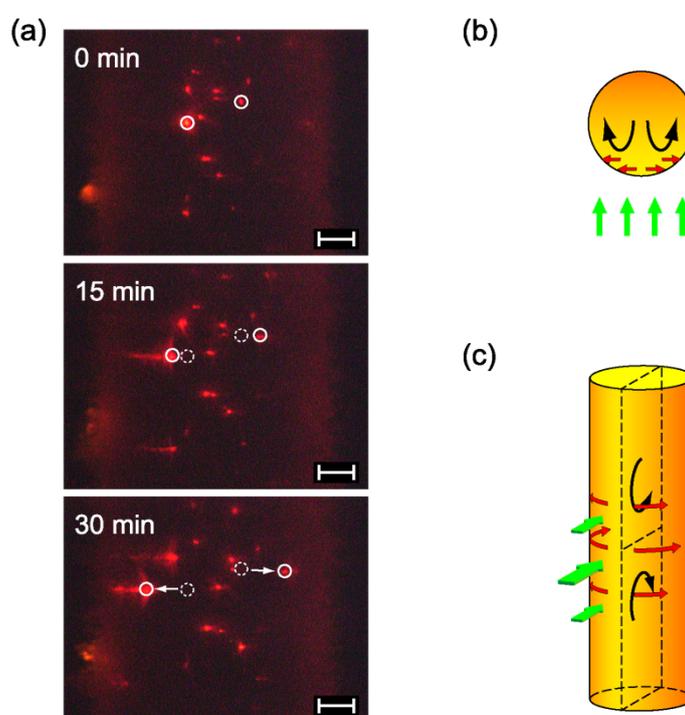
When the QDs-doped BF1AB fiber was irradiated, fluorescence of the QDs in the fiber existing at surface level in the irradiated area was observed. As shown in Figure 4a and supplemental video 1, several QDs were observed to move upon angled irradiation with H-polarized laser beam. On the other hand, such movement of QDs could not be observed when the fiber was vertically irradiated with H-polarized laser beam. These results were consistent with the result observed for QDs doped BF1AB film, where the mass flow was induced at surface level of the film upon angled irradiation with p-polarized laser beam while such mass transport could not be observed upon vertical irradiation [29]. Therefore, the bending motion of the fiber in the positive direction upon H-polarized laser beam could be interpreted as follows; when the fiber was irradiated, slight volume expansion was initially induced due to photo-thermal effect as shown by red arrows in Figure 4b, resulting in the slight bending of the fiber in the positive direction. The resulting slightly angled fiber was continuously irradiated with H-polarized laser beam, mass flow at the surface level of the irradiated area was induced as indicated by red arrows in the Figure 4c and such mass flow induced bending moment as indicated by a black arrow in the figure, resulting in further bending of the fiber in the positive direction.

Figure 4. (a) Photographs of fluorescence patterns of quantum dots (QDs)-doped BF1AB fiber upon angled irradiation using H-polarized laser beam. Scale bar: 10 μm . (b,c) Schematic illustration for plausible mechanism of the bending motion in the positive direction upon H-polarized laser beam. See text.



The next, the movement of the QDs was investigated viewed from the back of the irradiated surface upon V-polarized laser beam. As shown in Figure 5a and supplemental video 2, emitting positions of the QDs existing at surface level of the fiber were found to move toward both sides of the fiber perpendicular to the fiber axis, *i.e.*, parallel to the polarizing direction of the laser beam. The result could be understood that the surface of the fiber was irradiated with oblique angle, resulting in mass transport induced in the directions as indicated by red arrows in Figure 5b. The resulting mass transport was thought to produce the bending moment as indicated by black arrows in Figure 5c, resulting in bending of the fiber in the negative direction.

Figure 5. (a) Photographs of fluorescence patterns of QDs-doped BF1AB fiber upon irradiation using V-polarized laser beam viewed from the back of the irradiated surface. Scale bar: 10 μm . (b,c) Schematic illustration for plausible mechanism of the bending motion in the negative direction upon V-polarized laser beam. See text.



4. Conclusions

Photochromic molecular fibers composed of BMAB, DBAB, and NO_2 -BF1AB were fabricated. As well as BF1AB fiber we have previously reported, DBAB and NO_2 -BF1AB fibers exhibited photomechanical bending motions and the bending directions were controllable simply by altering the polarization directions of the laser beam. Thus the photomechanical bending motions observed in the present study were suggested to be general phenomena for azobenzene-based molecular fibers.

In-situ observation of the movement of emitting positions of QDots doped in the BF1AB fiber upon irradiation indicated that the photoinduced mass transport was induced at the surface of the irradiated area depending upon the polarization direction of the laser beam, which is consistent with the photoinduced mass flow at the surface level of the amorphous film of BF1AB upon angled irradiation with p-polarized laser beam. The photomechanical bending motions depending on the polarization

direction of the laser beam could be understood to be caused by photoinduced mass transport induced at the irradiated surface of the fiber.

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