Photocontrolled Manipulation of a Microscale Object: A Rotational or Translational Mechanism

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Abstract: In this paper the photocontrolled manipulation of solid materials on the surface of a liquid crystalline thin film is described. Three different types of films namely cholesteric liquid crystal (ChLC), compensated nematic liquid crystal (NLC) and nematic LC were used. The rotational and translational manipulation of the microscale solid object was induced by irradiation of light and mode of manipulation (either translational or rotational) was changed by changing the isomer of the azobenzene compound used to make the film. Rotational motion of the object was observed on the ChLC and compensated NLC films containing chirally pure azobenzene compound. The direction of rotational motion was controlled either by changing the optical isomer of the chiral azobenzene or by changing the irradiating light (from ultraviolet to visible). When racemic mixture of the chiral azobenzene compound was used, a translational motion of the object was observed. Even though the direction of the translational motion can be controlled by controlling irradiation position, more facile and precise manipulation of the objects was possible by spatially controlled irradiation of Ar+ laser and diode UV laser.

Keywords: azobenzene · liquid crystals · photochromism · surface chemistry

Introduction

The miniaturization of components for the construction of useful devices, which is an essential feature of modern technology, is currently pursued by a large downward (top-down) approach. This approach, however, leads scientists to manipulate progressively smaller pieces of matter. Several attempts of linear or rotary manipulation of micro-/nanoscale materials on surfaces have been recently reported.[1,2] Optical tweezers developed by Ashkin use the forces exerted by a strongly focused beam of light to trap and move objects ranging in size from tens of nanometres to tens of micrometers.[3] Light driven rotary manipulation of a microscale object by a molecular motor embedded in a liquid crystalline matrix was reported by Feringa et al.[4] Some groups have reported photocontrolled translational manipulation of a liquid droplet on a glass surface modified with a photo-switchable molecule, by generating a surface energy gradient.[5,6] Liquid crystalline elastomers (LCE) with an azobenzene moiety show the largest photomechanical effect, and are promising materials for applications as artificial muscles and actuators.[7,8] Very recently Ikeda et al. exploited the photomechanical effect of LCE with an azobenzene moiety to drive a plastic motor by light.[9] Palffy-Mohoray et al. reported movement of a photoactive LCE disk with a doped azobenzene compound which changes its shape during irradiation and can move in response to light.[10] Several groups have reported translational manipulation of a non-photoactive solid object (silica micro-particle or metal nanorod) on a surface[11] or through a microchannel,[12] where the motion was induced by conversion of chemical energy to kinetic energy. However, light driven translational motion of a solid object on a surface has remained a challenge for researchers in this field. Photochemical and electrochemical energy is preferable to chemical energy because of its ease of addressability, fast response time and reversible external control.[13] In addition, a chemically fuelled system suffers from problems such as addition of fresh reactants (“fuel”) and removal of waste product: use of light energy as fuel can overcome these problems.[13]
Liquid crystals are ordered soft materials consisting of self-organized molecules and the orientation of the molecules in a mesophase can be directed by the application of an external field (light, electric field, etc.). For this reason, LC materials have received a great attention for manipulation of micro-scale materials. Cholesteric (or chiral nematic) liquid crystals (ChLCs) are characterized by large, supramolecular, chiral organization, the chirality of which is indicated by the sign and magnitude of the cholesteric pitch. The pitch (\( p \)), the length of one turn of the cholesteric helix) is dependent on: 1) the concentration (\( c \)) of the dopant and 2) the helical twisting power (HTP) of the dopant, following Equation (1).

\[
p = \frac{1}{\text{HTP} \cdot c}
\]  

When a suitable ratio of chiral compounds possessing the ability to produce opposite right- and left-helical structures and to cancel one another is used, the result is known as a compensated NLC, and does not produce a helical structure. When one component of a chiral system constituting a compensated NLC is a photochromic compound such as an azobenzene, it may be possible to change the state of compensation through a change in the HTP by photoisomerization, so that a ChLC with a helical structure may be developed. If the racemic mixture of the chiral azobenzene compound is used there will be no helix formed as the helix formed by one isomer will be cancelled with that of other isomer. In this paper we used ChLC, compensated NLC and azobenzene doped LC films to study manipulation of microscopic object.

**Results and Discussion**

The chiral photochromic azobenzene compounds, non-photochromic compounds and host nematic liquid crystal (LC; Scheme 1) were used to study the manipulation of micrometer-sized glass rod on the LC surface. UV/Vis spectra confirmed that photoirradiation of the azobenzene compound with UV light (\( \lambda = 365 \text{ nm} \)) results in the formation of the cis isomer, and the reverse conversion from the cis to trans isomer occurs by irradiation with visible light (\( \lambda = 436 \text{ nm} \); see the Supporting Information, Figures S1 and S2). S-811 and R-811 reported to give left- and right-handed helical structures, respectively. A Ch phase was induced by mixing each chiral azobenzene compound and the nonphotochromic chiral compound in the host nematic liquid crystal (E44). The helical sense (helical rotatory direction) of the induced cholesteric liquid crystal was affected by the chirality of each chiral substituent. The helical pitch of each chiral azobenzene compounds was determined by Canos wedge method and the HTP was calculated by use of Equation (1). The determined HTP of S-811 and R-811 was 34.7 \( \times 10^4 \text{ m}^{-1} \text{mol}^{-1} \text{g}^{-1} \) E44 and 34.2 \( \times 10^4 \text{ m}^{-1} \text{mol}^{-1} \text{g}^{-1} \) E44. d-Azometh and l-azometh showed right- and left-handed helical structures, respectively. The calculated HTP of d-azometh and l-azometh was 49.4 \( \times 10^4 \text{ m}^{-1} \text{mol}^{-1} \text{g}^{-1} \) E44 and 49.0 \( \times 10^4 \text{ m}^{-1} \text{mol}^{-1} \text{g}^{-1} \) E44, respectively. The HTPs of both d-azometh and l-azometh compounds were decreased upon ultraviolet (UV) light (\( \lambda = 365 \text{ nm} \)) irradiation, as a result of photoisomerization of the azobenzene compound from trans to cis form. The calculated HTP of d-azometh and l-azometh after irradiation of UV light was 10.4 \( \times 10^4 \text{ m}^{-1} \text{mol}^{-1} \text{g}^{-1} \) E44 and 10.8 \( \times 10^4 \text{ m}^{-1} \text{mol}^{-1} \text{g}^{-1} \) E44 respectively. This large difference in HTP of d-azometh and l-azometh between its isomeric forms is essential for effective switching of liquid crystalline organization, which made it suitable for rotational manipulation of microscale materials.

**Rotational manipulation with cholesteric LC**: At first we made cholesteric liquid crystals (ChLC) by chiral azobenzene compound d-azometh/l-azometh doped in E44. When a thin film was made on the surface of glass slide having unidirectionally rubbed polyimide layer polygonal fingerprint texture was observed, that is typical for alignment of the cholesteric helix axis parallel to the surface (Figure 1). The pitch of the helix is depended on the concentration of the chiral compound, the higher the concentration, the lower the pitch. Thus the lines on the surface become narrower as the concentration of the chiral compound increases which is shown in the Supporting Information (Figure S3).

During irradiation of UV light (\( \lambda = 365 \text{ nm} \)) under the microscope the polygonal texture reorganized in a rotational (clockwise) fashion in response to the isomerization of the azobenzene compound and the subsequent modification of its helical twisting power. As the irradiation continues the width of the lines become wider and eventually faded out. To observe the movement of solid, few glass rods of typical diameter around 7 μm (with varying length) were sprinkled on the surface of the film, then UV and visible lights were alternatively irradiated on the film. In this case UV-visible light was irradiated homogenously on the film.

Upon UV light irradiation the rods rotated in clockwise direction, the same direction as the rotating cholesteric textures (Figure 1a–g). During visible light (\( \lambda = 436 \text{ nm} \)) irradiation...
tion the texture and the glass rod rotated in the counter-clockwise direction (Figure 1i–o) (for movie see Supporting Information video 18X). This reorganization of the texture generates a torque on the microscopic object that results in rotary motion. In this case no translational motion of the rod was observed. The angle of rotation was determined by measuring the change in angle of the glass rod during irradiation. Images were captured from the movie and the angle change was measured by comparing images before and after irradiation. In general, the angular displacement of the rod was increased with increasing the concentration of the azobenzene compounds (Figure 2). Initially the speed of rotation was faster, but the speed decreased as irradiation continued and eventually the rotation was stopped, due to the photostationary state of the azobenzene compound. For a specific concentration the speed of translation also increased with increasing intensity of the irradiating light (Figure 3).

When L-azometh instead of D-azometh was used as the doping azobenzene similar rotational behavior was observed. In this case the glass rod rotated to the counter-clockwise direction during UV light irradiation and clockwise direction during visible light irradiation. Thus, direction of rotational motion of the glass rod can be easily controlled either by controlling the isomer of the azobenzene compound or by changing the irradiating light (from UV to visible). In the Supporting Information, Figure S4 shows the rotational behavior of glass rod on the L-azometh doped E44 film, Figure S5, and Figure S6 shows the effect of concentration of L-azometh and intensity UV-visible light on angle of rotation, respectively.

Rotational manipulation with compensated NLC: Rotational behavior of the glass rod was also observed on the compensated nematic liquid crystal film containing a chiral azobenzene compound. The compensated NLC was prepared by mixing photochromic (chiral azobenzene compound) and a nonphotochromic chiral compound having opposite helical twisting ability to that of chiral azobenzene compound in E44 in the ratio that compensated the other's HTP. Upon irradiation of UV light, the compensated nematic phase breaks due to change in the helical twisting power of the photochromic compound with respect non-photochromic compound, consequently phase transition from the nematic phase to the cholesteric phase takes place (Figure 4).[16] When compensated NLC made by using D-azometh and S-811 was placed on a glass slide having unidirectionally rubbed polyimide layer, no helix observed on the glass substrate. Irradiation of UV light causes the changes in the HTP of D-azometh, so the compensated state of the films was broken, consequently helix can be observed on the film. The glass rod sprinkled on the film started to rotate clockwise as soon as the UV light irradiated on the film (Figure 4a–g). After some time, the cholesteric texture appeared (in this case after 1 s) the rotation continues for a while and eventually rotation was stopped when the photostationary state of the azobenzene compound was achieved. Again visible light irradiation caused the compensated NLC state to regenerate that is, the cholesteric texture disappeared upon visible light, and the glass rod rotated to the counter clockwise direction (Figure 4i–o).

In general, the angle of rotation of the rod was increased with increasing the concentration of the azobenzene compounds (Figure 5). Initially the speed of rotation was faster, but the speed decreased as irradiation continued and eventually the rotation was stopped, due to the photostationary state of the azobenzene compound. For a specific concentration the speed of translation also increased with increasing intensity of the irradiating light (Figure 6).

Similar rotational behavior of the glass rod was observed when the compensated NLC was made by using L-azometh
and S-811. In this case the glass rod rotated to the counterclockwise direction during UV-light irradiation and clockwise direction during visible light irradiation. Thus, the direction of rotational motion of the glass rod can be easily controlled either by controlling the isomer of the azobenzene compound or by changing the irradiating light (from UV to visible). Figure S7 shows the rotational behaviour of glass rod on the L-azomenth and R-811 doped E44 film. Figures S8 and S9 show the effect of concentration and intensity UV-visible light on angle of rotation, respectively.

**Observation of translational behavior**: In the previous sections, the rotational behaviour of glass rod was observed when chiral azobenzene compound was used. When the racemic mixture (dl-azomenth) of the chiral compound was used translational motion of the glass rod was observed. In the next section, the translation behavior of the glass rod with irradiation of UV-visible light, Ar\(^+\) laser and UV laser is described.

**Irradiation of UV-visible light**: During asymmetric\(^{[21]}\) irradiation of UV light (\(\lambda = 365\) nm) over the azobenzene doped film under microscope the sprinkled glass rod on the film always translated (speed 103 \(\mu\)m/min\(^{-1}\)) towards the irradiation position as a result of trans→cis isomerization. After UV light irradiation, when visible light (\(\lambda = 436\) nm) was irradiated the same rods translated (116 \(\mu\)m/min\(^{-1}\)) opposite direction to that of UV light irradiation that is, in this case the rods moved away from the irradiation position which was the result of cis→trans isomerization. Figure 7 shows the translational motion of the rods during irradiation of UV and visible light from right side, where the rod translated to right side during UV light irradiation and to the left side during visible light irradiation.

Symmetric irradiation of the film caused the movement of the rod in an arbitrary direction, so direction of translational motion cannot be controlled. Increasing concentration of azobenzene in the film caused more molecules to undergo photoisomerization; consequently the speed of translation of the rod was increased with increasing the concentration of azobenzene compound (Figure S10). Recently, Sen and co-workers\(^{[20]}\) developed the chemically fuelled translational motion of polystyrene microspheres connected to a catalytic Pt/Au nanomotor. The direction of motion was controlled by making use of the magnetic properties of the nickel segment in the Pt-Ni-Au-Ni-Au nanomotor, whereas we have eliminated the requirement for such a connection to a nanomotor and also the use of a magnet.

**Precise control of motion using Ar\(^+\) laser**: One of the most important challenges to the development of practical molecular machine is the development of fast and repetitive movement over longer time frames.\(^{[2]}\) As the translational motion of the rods during UV-visible was depended on the trans→cis isomerisation of the azobenzene compound the translation of the rods was stopped when almost all trans isomers change to cis isomer and vice versa. Another prob-

![Figure 2](image.png)

Figure 2. Changes in the angle of rotation of glass rod with time at different concentration of doped \(\alpha\)-azomenth during a) UV light irradiation (clockwise rotation) and b) visible light irradiation (counterclockwise rotation). Intensity of UV and visible light was 13.0 and 140 mWcm\(^{-2}\), respectively. Each point represents the average angle of at least three glass rods.

![Figure 3](image.png)

Figure 3. Changes in the angle of rotation of glass rod with time at different intensity of a) UV light (clockwise rotation) and b) visible light (counterclockwise rotation). Composition of the film was 2.0 wt% of \(\alpha\)-azomenth in E44. Each point represents the average angle of at least three glass rods.
Figure 4. Optical micrographs of rotation of glass rod on surface of compensated NLC film doped with d-azometh and S-811. Upon UV light irradiation ($\lambda = 365$ nm) the rod rotated clockwise (a–g), the rod rotated counterclockwise by visible light ($\lambda = 436$ nm) irradiation (i–o). Composition of the film d-azometh/S-811/E44 2.0:2.3:95.7, intensity of UV and visible light was 13.0 and 140 mW cm$^{-2}$, respectively.

Figure 5. Changes in the angle of rotation of glass rod with time at different concentration of doped d-azometh and S-811 during a) UV light irradiation and b) visible light irradiation. Intensity of UV and visible light was 13.0 and 140 mW cm$^{-2}$, respectively. Each point represents the average angle of at least three glass rods.

Figure 6. Changes in the angle of rotation of glass rod with time at different intensity of a) UV light and b) visible light. Composition of the film d-azometh/S-811/E44 2.0:2.3:95.7. Each point represents the average angle of at least three glass rods.
lem with translational motion of glass rod by UV-visible ir-
radiation was that precise control of direction was difficult
to achieve due to difficulty in changing the irradiation con-
dition such as direction, angle, position. These problems
were overcome by irradiation of Ar\(^+\) (\(\lambda = 488 \text{ nm}\)) laser
beam. Both \textit{trans} and \textit{cis} isomers absorb at 488 nm so both
\textit{trans–cis} and \textit{cis–trans} isomerisation can be simultaneously
induced by irradiation of Ar\(^+\) laser that is, Ar\(^+\) laser can re-
versibly form trans and cis isomers. Consequently, trans-
'\textit{tional motion of the glass rod was caused over infinite time}
without decrease in speed upon irradiation of Ar\(^+\) laser
beam. Precise control of direction of translation was easily
achieved by spatially controlled irradiation of Ar\(^+\) laser on
the film. As the laser beam is narrow (area of the beam
\(\sim 3 \text{ mm}^2\)) it was possible to change the irradiation position
easily. In this case the rods always moved away from the ir-
radiation position. It should be noted that it was not neces-
sary to irradiate laser beam on the rod, the movement of
the rod was observed upon irradiation of nearby regions of
the rod and the direction was controlled just by changing
the position of irradiation spot. If we place the irradiation
spot on left side of the rod, the rod moved to the right side,
after 44 s changing the irradiation spot to right side of the
rod caused movement to the left side; the rod moved to the
rear side upon placing the irradiation spot to front side and
moved back to the front side by changing the irradiation
spot to the rear side (Figure 8) (for movie, see Supporting
Information video 2 8X). So it was possible to move the rod
in any direction of interest and as soon as the irradiation po-
nosition was changed the direction of translation was changed
immediately.

The speed of motion was determined by measuring the
distance travelled by the glass rod in one minute. Images
were captured from the movie during irradiation and the
distance travelled was measured by comparing images
before and after irradiation. Several factors affected the
speed of motion, namely, intensity of the laser, the concen-
tration of the doped azobenzene compound. For a particular
film, the speed increased as the intensity of the laser in-
creased. The speed of translational motion as a function of
the laser intensity is shown in Figure 9a. No movement of
the rod was observed on pure E44 (azobenzene-free) film.

This indicates that \textit{trans–cis} isomerization of the azobenzene
compound induced translational motion of the rod. Conseque-
tly, the speed of motion increased (with few exceptions)
as the concentration of the doped azobenzene compound
at a specific laser intensity in-
creased. The dependence of the speed on the concentration of
the azobenzene compound is shown in Figure 9b.

Control of motion with UV laser: Since the absorptivity of
azobenzene molecule at 488 nm wavelength is not so high, it
was necessary to irradiate relatively high intensity of Ar\(^+\)
laser to induce the movement of the glass rod. However,
very fast movement of glass rod was observed when UV

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**Figure 7.** Optical micrographs of translational motion of a glass rod on the surface of an LC film doped with dl-azomenth (6 wt% in E44). The film was irradiated with UV/Vis light from the right side. a) Initial position of the rod. b) Upon irradiation with UV light (\(\lambda = 365 \text{ nm}\)), the glass rod moved to the right side, that is, to-
wards the irradiation position. c) The glass rod moved to the left side, that is, in the opposite direction, on vis-
oblight (\(\lambda = 436 \text{ nm}\)) irradiation. The length of the rod was 30 \(\mu\text{m}\) and diameter of the rod was about 7 \(\mu\text{m}\). On average, the speed of translational motion was 103 and 116 \(\mu\text{m min}^{-1}\) during UV and visible-light irradia-
tion, respectively. The intensity of UV and visible light was 13 and 140 mW cm\(^{-2}\), respectively.

**Figure 8.** Optical micrographs of the precise control of translational motion of glass rod by spatially controlled irradiation with an Ar\(^+\) laser. a),b) Laser irradiation from the left side of the rod resulted in motion of the rod to the right side and vice versa. c),d) Laser irradiation from the front side of the rod resulted in motion to the rear side and vice versa. e) The final position of the rod. Composition of the film 4 wt% dl-azo-
menth and the intensity of the laser was 240 mW cm\(^{-2}\). On average the speed of translational motion was 173 \(\mu\text{m min}^{-1}\).
laser (375 nm) was irradiated on the films. Unlike Ar+ laser/visible light irradiation the glass rods always translated towards the irradiation position during UV laser irradiation. The directional behavior is similar to that of UV light irradiation. Figure 10 shows the translational behavior of glass rod during irradiation of UV laser. On average, the speed of translation of the rod was 466 μm min⁻¹.

Possible mechanism: Liquid crystals are elastic medium, so that the volume of the LC can be easily changed by varying the temperature. When UV light was irradiated on the LC film, the photoisomerization of azo molecules from trans form having rod shape to cis form having bent shape was caused. The change in the molecular shape disrupts the molecular orientation of LC, and consequently photochemical phase transition occurs. It is known that the elasticity of a nematic LC decreases with increasing temperature in a LC phase near the isotropization temperature, so the elasticity of the area irradiated becomes lower than that of dark area. As a result, the glass rods move forward to irradiation position with UV light/laser. The recovery of the well ordered orientation of the LC molecules by subsequent visible light irradiation results in the movement of objects to the initial position. Therefore, the rate of movement became slower during long time irradiation, and came to a stop finally due to the photostationary state of the azobenzene molecule.

On the other hand, in the case of translational movement by irradiation with an Ar+ laser, the movement of the particle continued without stopping as long as the irradiation was continued (Figure 8). The absorbance of DL-azometh at 488 nm is much lower than that at 365 nm, however, not only the trans form but also the cis form has small absorption at 488 nm, so the irradiation at 488 nm causes trans-cis-trans photoisomerization cycle, and the amount of cis form produced with Ar+ laser is very small compared to that by irradiation of UV light. On the basis of the results, we expected that the driving force for the translation motion with Ar+ laser is different from the movement by UV and visible light irradiation.

Chono et al. reported that the movement of a small particle which was achieved by applying electric field to the LC system. This phenomenon was explained as velocity gradient induced by combination of anchoring effect of glass substrate and rotation of LC molecules under electric field. We guess that the translation with Ar+ laser is related to the re-orientation of LC molecules due to the trans-cis-trans photoisomerization cycle, and gradient of molecular motion between irradiated and dark regions. That is, the molecular motion of LC molecules in the irradiation site is activated due to the trans-cis-trans photoisomerization cycle, so we think the gradient of molecular motion is driving force of the translation motion of the glass rod.

Conclusion

Controlled movement of materials or molecules within the micro/nanometer range is essential in many applications of nanotechnology. Herein we showed the manipulation of a microscale object, this process may be applicable for biological material DNA, RNA, bacteria, nanoparticle. More precise control of the materials will be achieved if laser beam comparable/narrower to the size of the rods can be used. Even though continuous translational motion of the glass rod was achieved with Ar+ laser, rotational motion was continued for a short period of time, so it is necessary to design molecules for which continuous and faster rotation can be observed. Future studies with different liquid crystals, azobenzene compounds and irradiation conditions will allow us to get clear insight of the origin of the driving force for manipulation.

Experimental Section

The azobenzene compounds were synthesized following the previously described method. The films were made by dissolving an accurately weighed mixture (various wt% in E44) in THF. The solution was dropped onto a glass slide (25 × 20 mm) with a unidirectionally rubbed polyimide alignment layer. Evaporation of the solvent gave the azobenzene doped liquid crystalline film. Use of polyimide-rubbed glass allowed uniform films to be made, whereas attempts to make film on glass without polyimide/ rubbing were not successful. To observe the translational motion of solid objects a few glass rods of typical diameter about 7 μm
were sprinkled on the surface of the film, which was then irradiated with UV-visible light or an Ar+ laser beam. The angle of irradiation by light and the distance between the light source and film was about 45° and the distance between the light source and film was about 15 cm. The motion of the rods was observed using an optical microscope and video was recorded using a CCD camera.

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