Mass Transport

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Photocontrolled Translational Motion of a Microscale Solid Object on Azobenzene-Doped Liquid-Crystalline Films[**]

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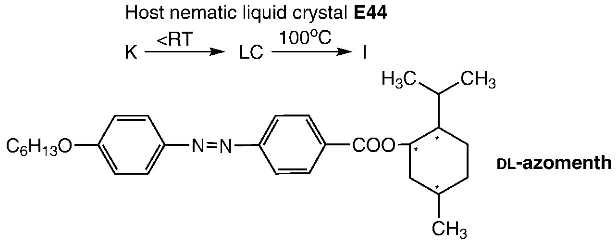
Several attempts to control linear or rotary motion of micro- or nanoscale materials on surfaces, in which the ultimate goal is the development of synthetic micro- or nanomachines, have been reported.[1,2] The light-driven rotary motion of a microscale object by a molecular motor embedded in a liquid-crystalline matrix has been reported by Feringa and co-workers.[3] Some research groups have reported the photocontrolled translational motion of a liquid droplet, which is located on a glass surface modified with a photoswitchable molecule, by generating a surface energy gradient.[4,5] Liquid-crystalline elastomers (LCEs) with an azobenzene moiety show the largest photomechanical effect, and are promising materials for application in artificial muscles and actuators.[6,7] Very recently, Ikeda and co-workers used the photomechanical effect of LCEs that incorporate an azobenzene moiety to drive a plastic motor by light irradiation.[8] Palffy-Mohoray and co-workers reported the motion of a photoactive LCE disk with a doped azobenzene compound that changes its shape during irradiation and can move in response to light.[9] Several research groups have reported the translational motion of a nonphotoactive solid object (silica microparticle or metal nanorod) on a surface[10] or through a microchannel,[11] where the motion was induced by conversion of chemical energy to kinetic energy. However, the light-driven translational motion of a solid object on a surface has remained a challenge for researchers in this field. Photochemical or electrochemical energy is preferable to chemical energy as a stimulus because of the ease of addressability, fast response time, and reversible external control.[12] In addition, a chemically fuelled system suffers from problems of addition of fresh reactants ("fuel") and removal of waste products—the use of light energy as fuel can overcome these problems.[12]

Herein, we demonstrate the translational motion of a microscale solid object (a polystyrene microsphere, PS) on the surface of a liquid-crystalline thin film. Motion of the microsphere was induced by irradiation with UV and visible light from a high-pressure mercury lamp or Ar$^+$ laser. The direction of motion depended on the direction and position of irradiation; directional control by using UV/Vis light irradiation was difficult, because of the difficulty of changing the direction and irradiation position of the high-pressure mercury lamp. However, the precise control of the direction of motion was easily achieved by irradiation with an Ar$^+$ laser. In addition, fast and repeated motion of the particles was observed over a long time. The speed of motion could be changed either by changing the intensity of the laser, or by changing the concentration of the doped azobenzene compound.

The photochromic azobenzene compound and host nematic liquid crystal (LC; Scheme 1) were used to study the translational motion of polystyrene microspheres on the LC surface. UV/Vis spectra confirmed that photoirradiation of the azobenzene compound with UV light ($\lambda = 365$ 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 ($\lambda = 436$ nm; see the Supporting Information).



Scheme 1. Host nematic liquid crystal (E44) and photochromic azobenzene (DL-azomenth) used to study translational motion.

During asymmetric irradiation of the azobenzene-doped film with UV light ($\lambda = 365$ nm; see the Supporting Information), PS particles sprinkled on the film were observed to move consistently towards the irradiation position at 88 μm min^{-1} (the observation was carried out by using a microscope). The motion is a result of *trans–cis* isomerization of the azobenzene-doped film. Following irradiation with UV light, when the same particles were irradiated with visible light ($\lambda = 436$ nm), they moved at 105 μm min^{-1} in the opposite direction, that is, away from the irradiation position, as a result of the *cis–trans* isomerization. Figure 1 shows the translational motion of the particles during irradiation by UV and visible light from the right side, in which the particle moved to the right side during UV irradiation and to the left side during visible-light irradiation (see Video 1 in the Supporting Information).[13] Since *trans*-azobenzene is the

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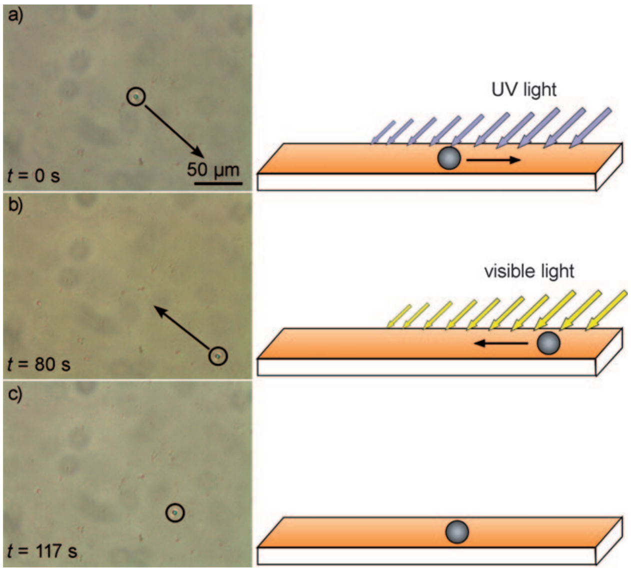

Figure 1. Optical micrographs of translational motion of a solid particle (PS) on the surface of an LC film doped with DL-azomenth (4 wt% in E44). The film was irradiated with UV/Vis light from the right side. a) Initial position of the particle. b) Upon irradiation with UV light ($\lambda = 365$ nm), the solid particle moved to the right side, that is, towards the irradiation position. c) The solid particle moved to the left side, that is, in the opposite direction, on visible light ($\lambda = 436$ nm) irradiation. The diameter of the PS particle was about 5 µm. On average, the speed of translational motion was 88 µm min^{-1} and 105 µm min^{-1} during UV and visible-light irradiation, respectively. The intensity of UV and visible light was 45 mW cm^{-2} and 65 mW cm^{-2}, respectively.

stable isomer, the *cis* isomer can revert to the *trans* isomer upon visible-light irradiation or by liberation of heat. We determined whether this thermal back reaction could induce translational motion of the solid particles. Interestingly, we observed motion of the PS particles but the speed was low (25 µm min^{-1}) compared to the motion induced by visible-light irradiation. In this case, the direction of motion was same as that induced by visible-light irradiation (see the Supporting Information for details of the UV/thermal motion of the particles). When the film was irradiated from the left side, the particle moved to the left side upon UV light irradiation and to the right side upon visible-light irradiation (see the Supporting Information). Recently, Sen and co-workers[14] developed the chemically fueled 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.

One of the most important challenges in the development of a practical nanomachine is the development of fast and repetitive motion over a prolonged time.[2] As the translational motion of the solid particles during UV/Vis irradiation arose from the *trans–cis* isomerization of the azobenzene compound, motion of the particles ceased when almost all of *trans* isomer was converted to the *cis* isomer, and vice versa.

As mentioned above, problems in achieving the precise control of direction of motion in translational motion of the solid particles were overcome by using an Ar$^+$ ($\lambda = 488$ nm) laser. Both the *trans* and *cis* isomers absorb light at 488 nm, so both *trans–cis* and *cis–trans* isomerization can be simultaneously induced by irradiation with the Ar$^+$ laser, that is, *trans* and *cis* isomers can reversibly be formed by using the Ar$^+$ laser. Consequently, translational motion of the solid particle was induced over indefinite time without decrease in speed upon irradiation with the Ar$^+$ laser. Precise control of the direction of motion was easily achieved by spatially controlled irradiation of the film with the Ar$^+$ laser. As the laser beam was narrow (area ≈ 3 mm^2), the position of irradiation, from which the particles always moved away, could easily be changed. It was not necessary to directly irradiate the particle with the laser. Motion of the particle was observed upon irradiation of regions near the particle, and the direction could be controlled merely by changing the position of the irradiation position. When the irradiation position was on the left side of the particle, the particle moved to the right side. After 85 seconds of irradiation, changing the irradiation position to the right side of the particle induced motion to the left side. The particle moved to the rear upon placing the irradiation spot to front side, and moved back to the front by changing the irradiation position to the rear (Figure 2 and Video 2 in the Supporting Information). Thus, as soon as the irradiation position was changed, the direction of motion immediately changed and it was possible to move the particle in any direction of interest.

The speed of motion was determined by measuring the distance traveled by the polystyrene particle in one minute. Images were captured from the movie during irradiation and the distance traveled was measured by comparing images before and after irradiation. The speed of motion varied with the intensity of the laser and the concentration of the doped azobenzene compound. For a particular film, the speed increased as the intensity of the laser increased. The speed of translational motion as a function of the laser intensity is shown in Figure 3a. No particle motion was observed on pure E44 (azobenzene-free) film. This indicates that *trans–cis* isomerization of the azobenzene compound induced translational motion of the particle. Consequently, the speed of motion increased (with few exceptions) as the concentration of the doped azobenzene compound at a specific laser intensity increased. The dependence of the speed on the concentration of the azobenzene compound is shown in Figure 3b. Polarization of the Ar$^+$ laser had no significant effect on the speed, that is, little change of speed was observed in the case of linearly polarized (polarizing angle 0°, 45°, and 90° with respect to rubbing direction), circularly polarized, and nonpolarized lasers (see the Supporting Information). There was also no significant effect of the rubbing direction on the motion, that is, similar motion behavior (speed and direction) was observed during irradiation parallel and perpendicular to the rubbing direction (see the Supporting Information).

The controlled motion of materials or molecules within the micro- or nanometer range is essential in many nanotechnological applications.[15] The results presented above

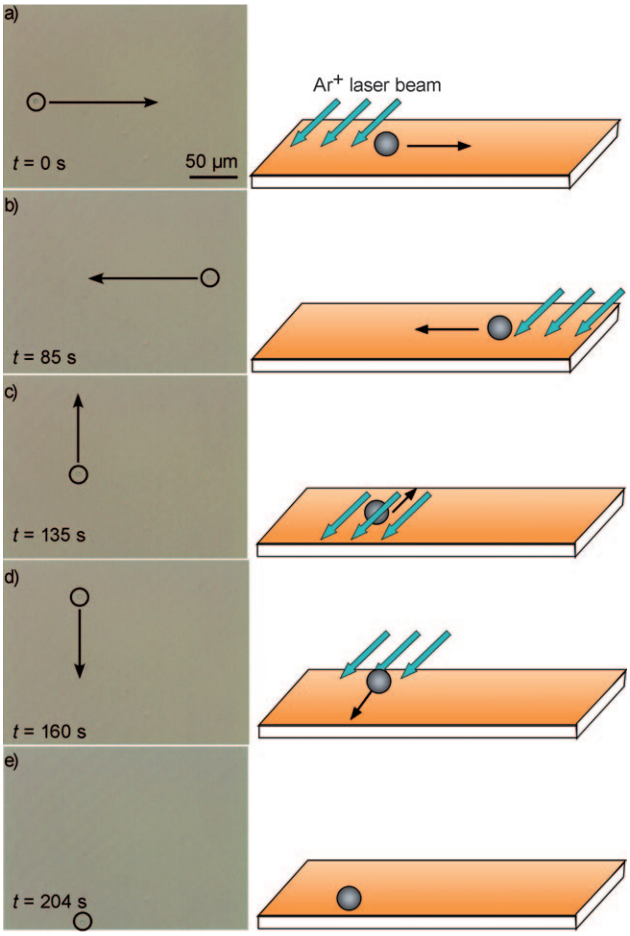

Figure 2. Optical micrographs of the precise control of translational motion by spatially controlled irradiation with an Ar$^+$ laser. a, b) Laser irradiation from the left side of the particle resulted in motion of the particle to the right side and vice versa. c, d) Laser irradiation from the front side of the particle resulted in motion to the rear side and vice versa. e) The final position of the particle. The intensity of the laser was 130 mW cm^{-2}. On average the speed of translational motion was 160 µm min^{-1}.

represent the first observation of controlled translational motion, which is driven entirely by light, of a solid object on the surface of liquid-crystalline films. The speed of the motion was controllable by changing the intensity of the laser or the concentration of the azobenzene compound. The precise nature of the driving force for the translational motion is still not clearly understood. One possibility is that motion of the particle was caused by a surface energy gradient[4] created during irradiation, or by reorientation of the LC molecule induced by *trans–cis* isomerization, or by a combination of both effects. Even though the origin of the driving force is not clear, light-driven translational motion of solid objects will open the way for applications in the field of microfluidics, for example, lab-on-a chip technology, diagnostics, or immunoassays.

Experimental Section

Films were prepared by dissolving an accurately weighed mixture (various wt % of DL-azomenth 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 films on glass without polyimide rubbing were not successful. The thickness of the films was about (25 ± 5) µm. To observe the translational motion of solid objects a few PS particles of typical diameter about 5 µm were sprinkled on the surface of the film, which was then irradiated with UV/Vis light or an Ar$^+$ laser. The angle of irradiation was about 45° and the distance between the light source and film was about 15 cm. The motion of the particles was observed by using an optical microscope and videos were recorded with a CCD camera.

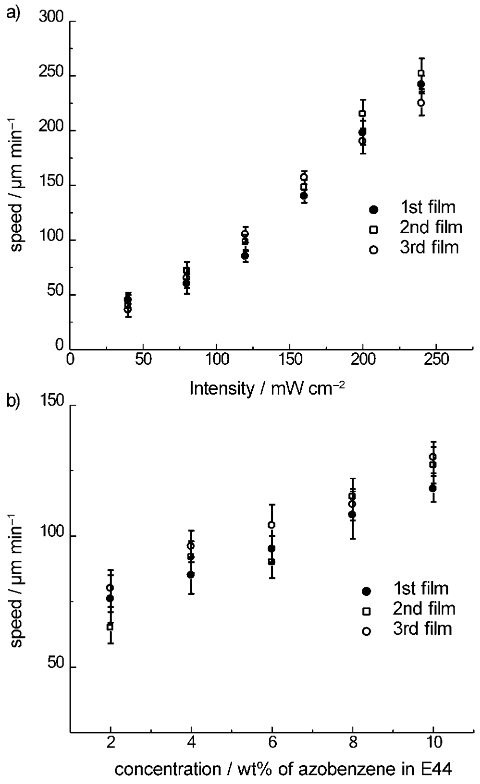

Figure 3. a) Effect of laser intensity (linearly polarized) on the speed of translational motion (film composition: 4 wt % DL-azomenth in E44). b) Effect of the concentration of doped azobenzene compound on particle speed (intensity of laser 120 mW cm^{-2}). Each point represents the average speed of at least three particles.

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