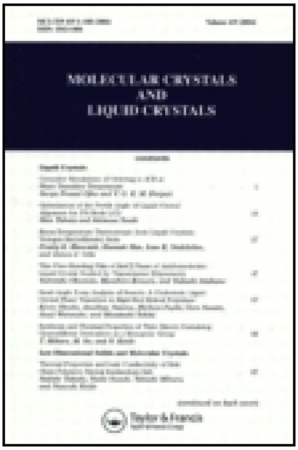

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# Light-Driven Organized Layer Materials

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# Light-Driven Organized Layer Materials

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*Organized molecular systems provide alluring light-driven actuation systems. They can be migrated or deformed themselves or control states of other ordered materials. This paper presents our two recent topics on light-driven organized monolayers and thin films comprising photochromic azobenzene-containing liquid crystalline polymers; i) photo- alignment of nanochannels in mesoporous silica film, and ii) light-triggered instant mass migration in a thin film state, which can be utilized as a conveyance system for micropatterning of light-inert molecules and materials.*

**Keywords:** azobenzene; mesoporous materials; photoinduced mass transport; photoresponsive monolayer

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## INTRODUCTION

Research on azobenzene (Az)-containing polymeric films has exploded during the past few decades, and it is continuing to be a very active area of materials chemistry [1–3]. Azobenzene is perhaps the most frequently used photochoromic unit to be incorporated in molecular assemblies and organized polymeric materials. Azobenzene (Az)-containing polymers provide fascinating photoresponsive actuation systems [4]. When they are organized at interfaces, the motion of Az unit occurring at a molecular (sub-nano) scale can be transferred and amplified to larger scales of materials. Also, cooperative motions in the isomerization process can lead to micrometer-scale mass transfer. This paper summarizes our recent progresses on the dynamic properties of Az-containing polymers.

## ALIGNMENT CONTROL OF NANOCHANNELS BY POLARIZED LIGHT

### Alignment Procedures

Liquid crystals can be aligned on a photochromic layer irradiated with polarized light via the optical anisotropy effect [5]. This principle was successfully applied to photoalignment of nanochannels of a mesoporous silica film via multiple transfer steps from a photo-oriented Az monolayer via orientation of a polysilane thin film and finally to surfactant-templated silica thin film (Fig. 1) [6,7]. At the first stage, a monolayer of poly(vinyl alcohol) (6Az10-PVA) having an Az side chain on a quartz substrate was prepared by the Langmuir-Blodgett method. Onto this photoresponsive monolayer, linearly polarized light (LPL) was illuminated, resulting in the photoalignment of the azobenzene side chain orthogonal to the polarization plane. A spincast film of poly(di-*n*-hexylsilane) (PDHS) was subsequently prepared onto this photooriented Az monolayer. After crystallization, the PDHS film exhibited a strong in-plane optical anisotropy. The polarized absorption spectra reveals that the Si backbone is highly aligned perpendicular to the polarization plane of the actinic light. The aligned direction of PDHS main chain agrees with that of the azobenzene orientation on the substrate [8,9]. The mesoporous silica film formed with a template of rod micelles of cetyltrimethylammonium chloride. The deposition of silica thin film was performed at room temperature for one week.

### Characterizations

In the optical microscopic images of the deposited surfactant/silica hybrids, uniaxially aligned elongated particles with widths of a

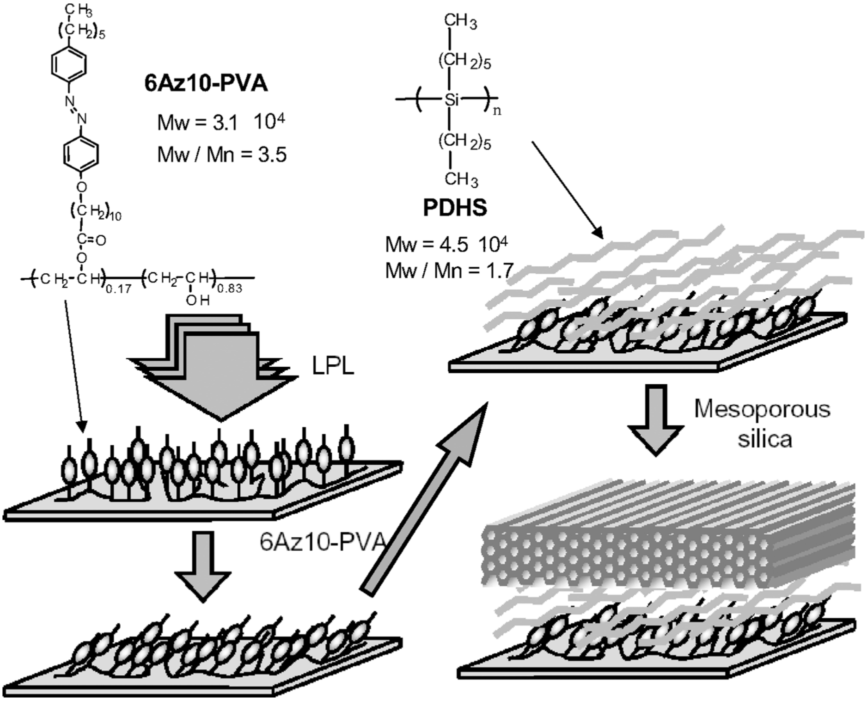


**FIGURE 1** Schematic illustration of photoalignment method of mesoporous silica film.

micrometer range were observed. The orientation of each particle was highly aligned parallel to each other, the direction of the longer side of silica particles being parallel to the polarization plane of the actinic LPL.

Decisive evidence for the formation of uniaxially aligned mesochannels was obtained by transmission electron microscopy (TEM). The two TEM photographs in Fig. 2 depict the cross-sectional structure of the as-synthesized surfactant/silica hybrid film observed in the two directions orthogonal to each other [7]. Figure 2a shows the image when the film is sliced parallel to the direction of the actinic polarized light. The hexagonal structure of the mesochannels is clearly visualized through overall thickness of the film. On the other hand, when the film is sliced perpendicular to the direction of the actinic polarized light, the lines with a periodicity of ca. 4 nm running parallel to the substrate were observed (Fig. 2b). The periodic length coincides well with that of the hexagonal spacing obtained by X-ray diffractometry.

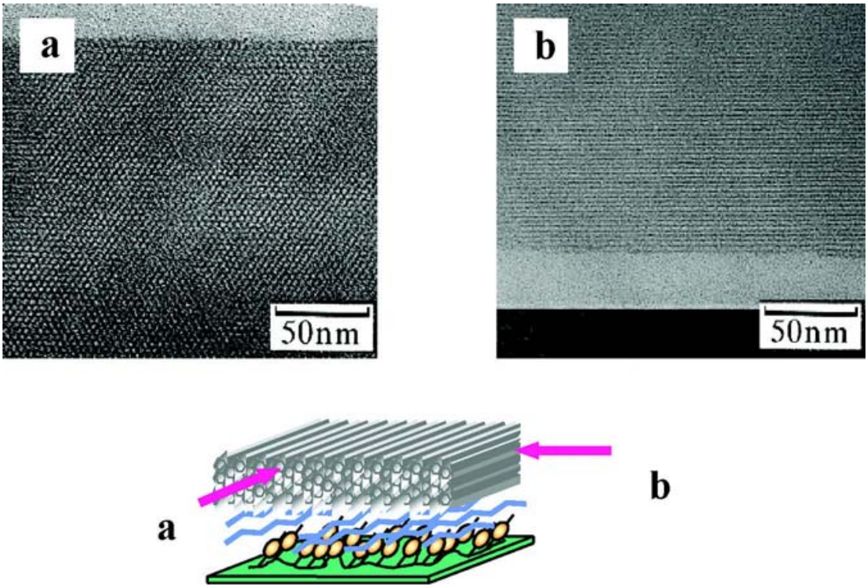


**FIGURE 2** Transmission microscopic images of photoaligned mesoporous channels. a and b corresponds to the viewing directions shown in the scheme below.

The cylindrical structure of the mesochannels was fully stretched straight in the film.

Patterning in terms of mesochannel orientation could be achieved when two polarized beams orthogonal to each other were used [7]. The discrimination of the channel orientation was suggested by the direction of cracks formed in the film. It is already confirmed that X-ray measurements and optical microscopic observations revealed that the extended cracks are formed orthogonal to the channel direction [7].

## LIGHT-TRIGGERED RAPID MASS MIGRATION

Surface relief grating (SRG) formed via the irradiation with an interference pattern of coherent light has attracted considerable attention [10–12]. A great deal of data has been accumulated for amorphous polymers with a pendant push-pull type azobenzene showing a glassy state in experimental conditions (room temperature) [13], however little knowledge has been obtained for polymers possessing an Az with little electrical modification showing a liquid crystalline state at this temperature.

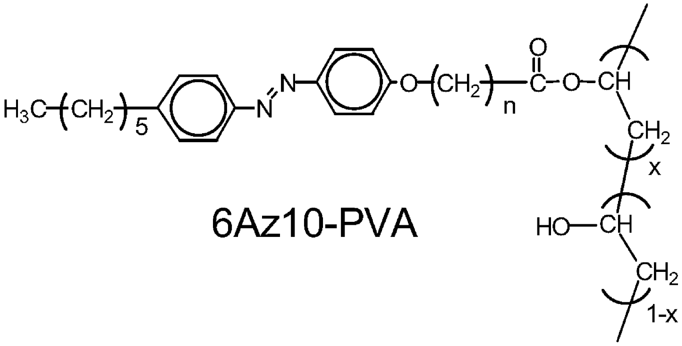
## Outline of Rapid Mass Transport

We found a unique mass migration behavior in liquid crystalline binary component materials comprised of 6Az10-PVA and a low-molecular-mass liquid crystal (4′-pentyl-4-cyanobiphenyl, 5CB) (Fig. 3) [14]. The hybrid films were irradiated with non-polarized UV (365 nm) light in advance to attain a cis-rich photoequilibrated state (UV light treatment). Starting from this state, the irradiation that induces the film migration was performed by argon ion laser beam (488 nm) which also induces back reaction to the transform. The growth of the first-order diffraction efficiency monitored with a He-Ne laser and morphological evaluation by AFM indicate that the mass migration is attained at very small dose levels as less than 100 mJ cm$^{-2}$, which is comparable to typical photopolymer systems for photoresists. Here, the energy level is *three orders of magnitude smaller* than those required for conventional amorphous polymer systems. The same behavior was also observed for copolymers having an Az side chain and an oligo(ethylene oxide) [15]. Interestingly, these films had no polarization dependency with respect to the transport direction [16].

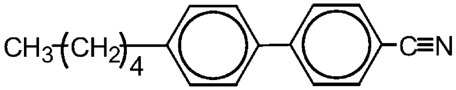
## Conveyer Actions

Thus far, applications of photoinduced migrations considered have been almost limited to utilizations of resulting static relief structures. They involve holographic recording, phase mask, LC alignment, waveguide couplers, fabrication of intricate surfaces etc. [1,13], In our rapid mass migration system, the dynamic motion itself can be a valuable function. Here, an application as “molecular conveyer” for patterning of light-inert (non-photoresponsive) functional materials is proposed [17,18]. A schematic illustration of this concept is displayed in Fig. 4. First, the guest materials are distributed randomly with no particular care, and the photo-triggered migration gathers the guest to target positions according to the patterning framework of illumination.

Conveyer actions for a dyestuff is demonstrated here as an example. A blue rodlike diaminoanthraquinone-type dye was embedded into the hybrid film of 6Az10-PVA and 5CB. At higher dye content, e.g. 10 mol % of the LC molecule, the UV irradiation followed by dark adaptation at room temperature for a day leads to a growth of dendritic crystals of the dye (Fig. 5a). When the crystallization was performed after the photoinscription of the lined relief (18 μm width in this case), the direction of dye organization was restrained and aligned along the relief structure (Fig. 5b). After sufficient crystallization at room temperature, the



6Az10-PVA



5CB

FIGURE 3 Chemical structure of the Az containing polymer (6Az10-PVA) employed and liquid crystal molecule (5CB).

protruding line showed a high optical anisotropy. The polarized optical-microscope image (Fig. 5c) revealed that the dichroic dye was aligned in the direction of the inscribed line. As shown, the absorption moment of the dichroic dye was highly aligned parallel to the direction of the inscribed line. Most probably, the orientational anisotropy is induced by a uniaxial growth in the diffusion-limited crystallization restricted in one dimensional geometry.

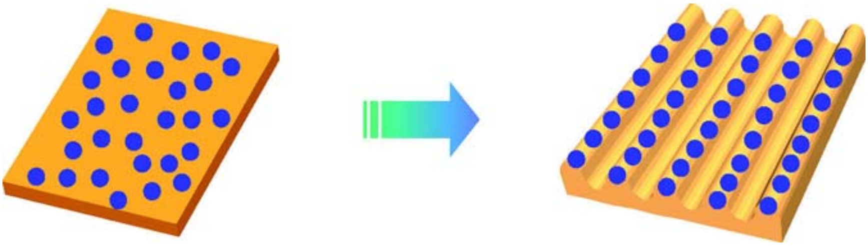


FIGURE 4 Schematic illustration of patterning of functional materials via the conveyance actions of photo-triggered mass migration in the Az polymer film.

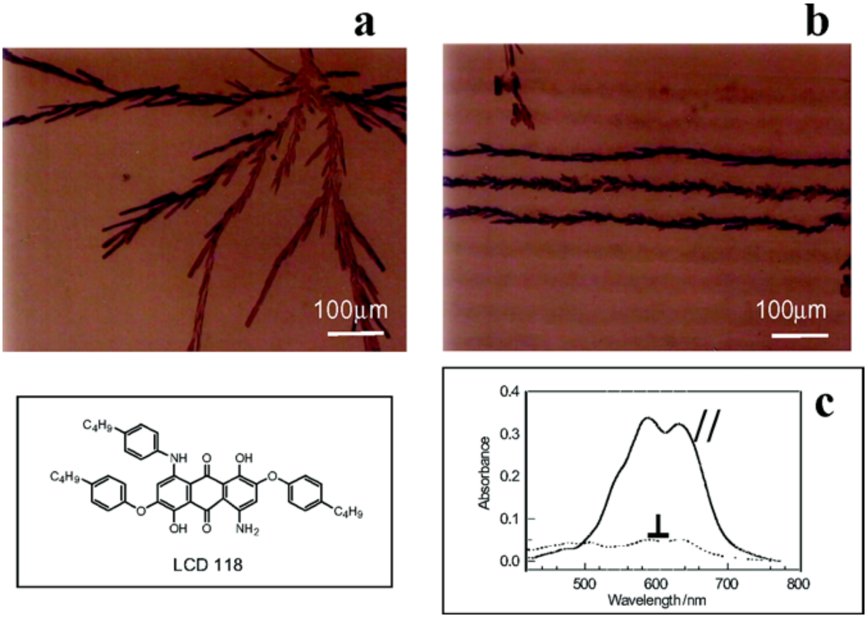


**FIGURE 5** Organization of crystallized dye molecule (LCD 118) on the 6Az10-PVA/5CB hybrid film without (a) and after patterned illumination through a line photomask (b). The polarized absorption spectra taken for b indicates a highly ordered alignment of dye molecules along the inscribed line (c).

Application of the mass conveying principle is not limited to low-molecular-mass molecules; polymer and larger materials such as poly(alkylthiophene) [18] and, semiconductor nanocrystals (NCs) of 6 nm diameter with $6 \times 10^5\,\mathrm{g\,mol^{-1}}$ mass weight [17] could be also conveyed. Accumulation of these materials can be detected by fluorescence microscope. After a short light exposure through a grating photomask, surface relief undulations were clearly formed. Such conveying action may be widely applicable to other kinds of functional materials that are themselves inert to light. A great advantage to use the rapid migration system can be the requirement of small amounts of light, which would not damage the host materials.

## CONCLUSION

We demonstrated here that proper designs of monolayer or thin films composed of photochromic Az polymers provide alluring molecular control systems for material science and technology. In the former part, a new example of surface-mediated material controls is demonstrated. Surface photoalignment of liquid crystals has been well recognized. Here, such control principle was extended to a rigid inorganic material. In the latter part a new patterning method of functional materials utilizing the conveyance motion of photo-triggered rapid mass migration is proposed. We anticipate that the versatility of conveyer actions that require no solvent-development will find new opportunities in micrometer level processing.

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