Manipulation and assembly of small objects in liquid crystals by dynamical disorganizing effect of push-pull-azobenzene-dye

OPEN

Manipulation and assembly of small objects in liquid crystals by dynamical disorganizing effect of push-pull-azobenzene-dye

Seiji Kurihara[1,2,3], Kazuhiro Ohta[1], Takahiro Oda[1], Ryo Izumi[1], Yutaka Kuwahara[1,3], Tomonari Ogata[3,4] & Sun-Nam Kim[1]

[1]Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto, 860-8555, Japan, [2]CREST, JST, K's Gobancho, 7 Gobancho, Chiyoda-ku, Tokyo, 102-0076, Japan, [3]Kumamoto Institute for Photo-Electro Organics (PHOENICS), 3-11-38 Higashimachi, Higashi-ku, Kumamoto, 862-0901, Japan, [4]Innovative Collaboration Organization, Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto, 860-8555, Japan.

The phase transition of a nematic liquid crystal containing a push-pull azobenzene dye could be induced efficiently during irradiation with visible light. The dynamical disorganizing effect of the push-pull azobenzene dye on the liquid crystalline order through its *trans-cis-trans* photoisomerizaion cycle under visible light was contributed to the efficient phase transition. Then, the effects of light irradiation on the motion of small objects dispersed in the liquid crystals containing the push-pull azobenzene were explored, and the manipulation and assembly of those objects were successfully achieved in the nematic phase but also in the smectic phase. The combination of the photo-controlled dynamical change in the liquid crystalline order and the intrinsic self-assembly property of a liquid crystal is promising for use in technologies that require not only the organization of small objects but also the photo-driving of nano- and micro-sized mechanical materials.

The dispersion of colloidal particles in a nematic liquid crystal (LC) causes long-range distortion of the orientational order of the nematic LC around the colloidal particles, known as topological defects[1–10]. Much effort has focused on the formation of one- and two-dimensional (1-D and 2-D, respectively) periodic structures that consist of colloidal particles in a nematic LC through the long-range interaction between the colloidal particles with respect to their topological defects[1,2,4,8,10]. Recently, Musevic and Tatarkova independently reported the motion and trapping of small colloidal particles in a nematic LC using an infrared laser to induce a thermally disordered region[6,9]. The long-range interaction mediated by the LC field between the colloidal particles and the thermally induced disordered region is considered to contribute to the motion and trapping of the colloidal particles. Consequently, even small particles with refractive indices lower than that of the surrounding medium can be moved and trapped, in contrast to the use of optical tweezers[11]. Therefore, one can assume that the thermally induced motion of the colloidal particles could be utilized to form 1-D and 2-D periodic structures, regardless of the relative refractive indices of the small objects and their surrounding medium.

However, Yamamoto and co-workers described the manipulation of polymers in a nematic LC via the photo-isomerization of azobenzene dye, which provides spatial variation in the LC order[12]. Azobenzene dyes are known to exhibit reversible photoisomerization between their *trans* and *cis* forms when irradiated with an appropriate wavelength of light or when heated. The rod-shaped *trans* form of azobenzene dyes is thermodynamically stable, whereas the bent *cis* form undergoes thermal reverse isomerization[13–15]. When UV irradiation of LCs that contain azobenzene dyes is used to initiate a photoisomerization from the *trans* form to the *cis* form, the phase transition temperatures of the LCs are reduced due to the disorganizing effect of the *cis* form that arises from its molecular shape, causing a phase transition to other LC phases or an isotropic phase[16,17]. These findings indicate that the spatial variation of the LCs can be precisely controlled through the photoisomerization of azobenzene dyes in the LCs by varying the light intensity and shape, the irradiation temperature, the concentration of the azobenzene dyes, the phase transition behavior of the host LCs, and other factors. Based on the results reported by Musevic, Tatarkova and Yamamoto, one might conceive the manipulation and assembly of small particles in a nematic LC
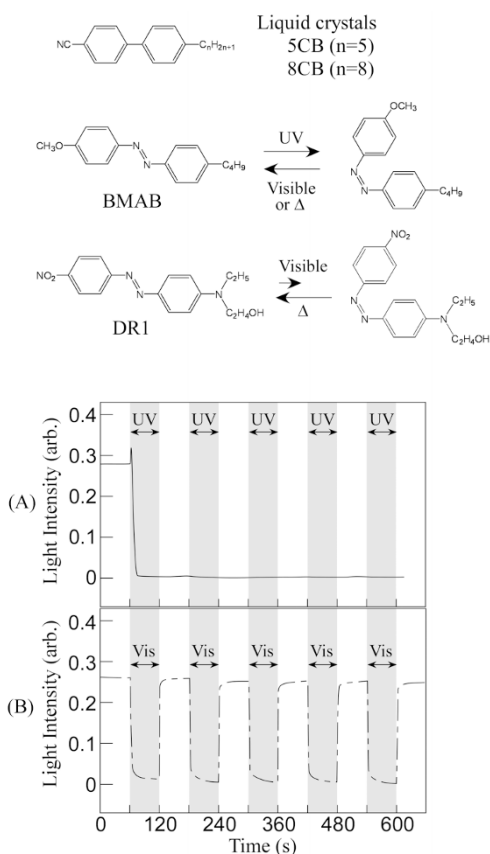
Figure 1 | **Changes in the light intensity transmitted by a He-Ne laser through BMAB/5CB in a 1-μm glass cell (A) and DR1/5CB in a 50-μm glass cell (B) between crossed polarizers under irradiation with UV (375 nm, 13 mW) or Ar+ (488 nm, 15 mW) lasers at 27°C.**

utilizing the disorganizing effect of the azobenzene dyes on the LC order. Contrary to expectation, no manipulation could be achieved by the simple photochemical disorganizing effect of the azobenzene dyes; however, we found that various small objects could be manipulated using a push-pull azobenzene dye under irradiation with visible light alone to cause the *trans–cis–trans* photoisomerization cycle in not only a nematic LC but also a smectic LC. Here, we describe first the dynamical disorganizing effect of the *trans–cis–trans* photoisomerization cycle of a push-pull azobenzene dye on the LC order by comparing it with non-push-pull azobenzene dyes. We then demonstrate the precisely controlled manipulation and assembly of small objects such as polystyrene spheres, glass rods and mica sheets in both the nematic and smectic LCs through a photochemically induced spatial variation and control of the LC order.

Results

We used two azobenzene dyes, BMAB and DR1, with 5CB as a host nematic LC (Fig. 1). The photoisomerization behavior of the azobenzene dyes, in particular, the reverse isomerization from the *cis* form to the *trans* form, is dependent on their molecular structure[14,15] and alters the quantity of *cis* azobenzene dye in a photostationary state. The irradiation of BMAB in 5CB with 365 nm light provided a photostationary state consisting of approximately 10% *trans*-BMAB, whereas no change in the absorption spectra was observed for DR1 in 5CB, indicating extremely low quantities of the *cis*-DR1 in the photostationary state due to the thermally rapid reverse isomerization from the *cis* form to the *trans* form (Supplementary Fig. S1A)[14,15].

A mixture of the host nematic LC, 5CB, and an azobenzene dye, BMAB (4.6 mol%) or DR1 (0.1 mol%) was injected into homogeneous

glass cells with cell gaps of 1, 5 and 50 μm. The cells consisted of two parallel glass plates coated with a polyimide and rubbed to obtain a homogeneous alignment. The mixture in the homogeneous glass cell was thermostated and placed between two crossed polarizers, whose polarizing directions were set at an angle of 45° with respect to the rubbing direction (Supplementary Fig. S2). The change in the molecular orientation of the 5CB molecules was explored by measuring the light intensity transmitted by a He-Ne laser (633 nm, CVI Melles Griot, USA) as a monitoring light source both with and without the light irradiated onto the sample, which was used to produce the photoisomerization of the azobenzene dye at 27°C. By monitoring the light transmitted through both the BMAB/5CB and DR1/5CB mixtures in the glass cell, both mixtures were found to be in the nematic phase before irradiation at 27°C. As shown in Fig. 1A, the transmitted light intensity of the BMAB/5CB mixture in the 1-μm glass cell decreased significantly during irradiation with a UV diode laser (375 nm, 5 mW, Kikoh Giken), and the intensity did not increase again after the irradiation of the mixture ceased, indicating that a photochemical phase transition had occurred. Actually, the phase transition temperature of the BMAB/5CB mixture was lowered during irradiation with the UV laser, and the temperature decreased with increasing BMAB concentration under UV irradiation (Supplementary Fig. S3). The irradiation of the BMAB in 5CB with 365 nm light led to the isomerization of more than 90% of the BMAB molecules to the *cis* form in the photostationary state. The recovery of the *trans*-BMAB in 5CB at 27°C required more than 10 h (Supplementary Fig. S1B). The large quantity of *cis*-BMAB and its stability contributed to the photochemical phase transition, which arose from the disorganizing effect of the *cis*-BMAB (Fig. 2B).

Unlike that with the BMAB/5CB mixture under UV irradiation, the monitoring light intensity through the DR1/5CB mixture in the 50-μm glass cell decreased during irradiation with an Ar+ laser beam at 488 nm (National Laser Co., USA) at 27°C and increased after the irradiation was discontinued, as shown in Fig. 1B. The absorbance of the DR1/5CB mixture in the 50-μm glass cell at 488 nm was approximately 0.4, which was roughly equal to that of the BMAB/5CB mixture at 375 nm in 1-μm glass cell. Observations made with a polarized microscope revealed that a phase transition to an isotropic phase occurred during the irradiation; the phase transition to the isotropic phase was only produced by irradiation with an Ar+ laser. For the BMAB/5CB mixture, approximately 2 mol% of the *cis*-BMAB was required to lower the phase transition temperature to 27°C (Supplementary Fig. S3). In contrast, the DR1 concentration in the DR1/5CB mixture was only 0.1 mol%. Accordingly, the quantity of *cis*-DR1 produced during the light irradiation was obviously less than the initial DR1 concentration and was most likely considerably below 0.01 mol% because of a rapid reverse reaction to the *trans* form[15]. Thus, the phase transition of the DR1/5CB mixture under visible light irradiation is not simply related to the decrease in the phase transition temperature, which depends on the quantity of the *cis* form produced in the host LC. To elucidate the thermal effects of the light irradiation that occur in addition to the disorganizing effect, the change in the transmitted light intensity of an NK-1951/5CB mixture in the 50-μm glass cell was explored via irradiation with an Ar+ laser. The NK-1951 (Supplementary Fig. S4) is a non-photochromic dye, which means that the absorbed light energy is expected to be converted into thermal energy. When the absorbance of the NK-1951/5CB mixture at 488 nm was adjusted to agree with that of the DR1/5CB mixture, little change was observed in the transmitted light intensity (Supplementary Fig. S4). Based on these results, it is likely that the phase transition during visible light irradiation is caused by the dynamical disorganizing effect of the DR1 due to its *trans–cis–trans* photoisomerization cycle. The *cis* form of the DR1 in some solvents is reported to revert to the *trans* form on a time scale of milliseconds to seconds depending on the solvent properties[14].
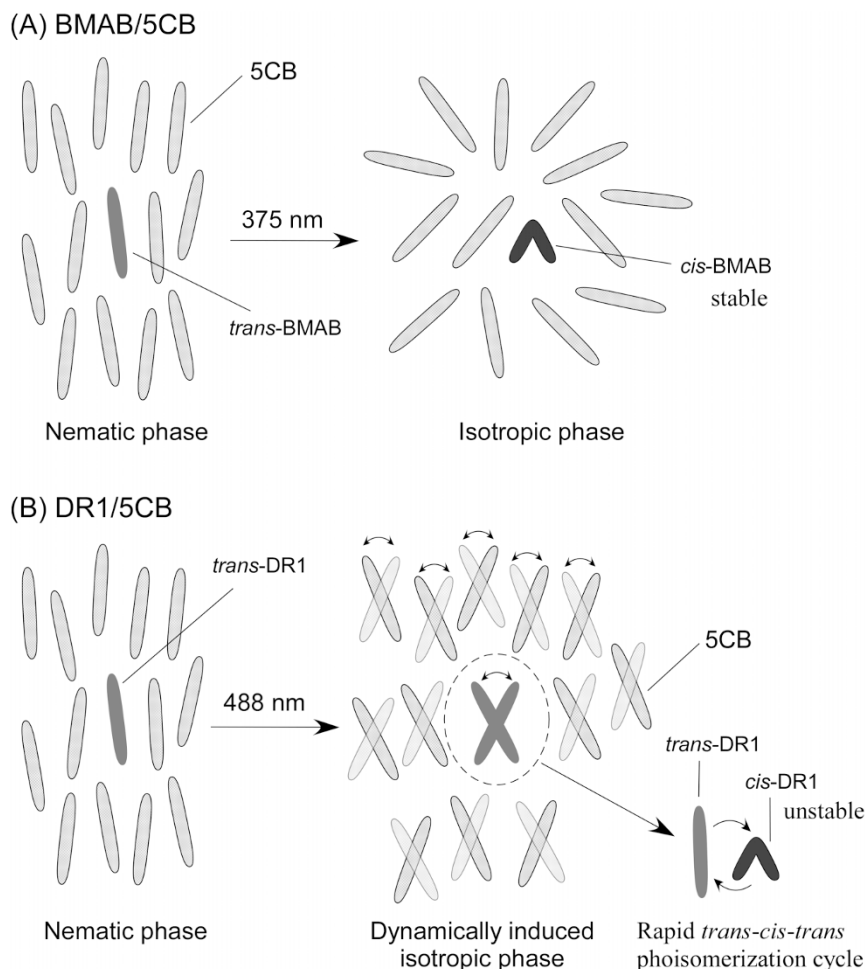
Figure 2 | Changes in the molecular orientation of the BMAB/5CB (A) and DR1/5CB (B) under irradiation with UV (375 nm, 13 mW) or Ar+ (488 nm, 15 mW) lasers.

Although the exact rate constant of the *cis*-to-*trans* thermal isomerization of the DR1 in 5CB is unknown, one can expect that each DR1 molecule is forced to reversibly and continuously change its molecular shape as it does in other solvents based on the observation that the absorption spectra of the DR1 in 5CB was unaltered during visible light irradiation. The continuous change in the molecular shape of the DR1 molecules during the *trans*–*cis*–*trans* photoisomerization cycle spontaneously causes the 5CB molecules to fluctuate around the DR1 molecules beyond the thermal orientational fluctuation of the 5CB molecules, although the average quantity of *cis*-DR1 produced during irradiation with visible light is low (Fig. 2B). Thus, the phase transition can be caused by a much smaller quantity of DR1 compared with that of BMAB.

The subsequent effect of the photochemically induced variation in the LC order on the motion of the micron-sized objects dispersed in 5CB was investigated as follows: We used glass rods with lengths of approximately 30 μm and diameters of approximately 8 μm as the objects. The glass rods were dispersed in the BMAB/5CB and DR1/5CB mixtures, and the resulting mixtures, G-R/BMAB/5CB and G-R/DR1/5CB, were injected into the 50-μm-thick homogeneous glass cell. We first irradiated the G-R/BMAB/5CB mixture in the homogeneous glass cell with a focused UV diode laser at 25°C to induce a phase transition in the mixture from the nematic phase to the isotropic phase. The laser beam, moved along the surface of the cell, had a diameter and intensity of approximately 100 μm and 13 mW, respectively. An isotropic phase appeared during the UV irradiation (Fig. 3), although the mixture was in the nematic phase at 25°C before irradiation. The glass rods dispersed in the mixture were found to move toward the isotropic region and collect at a nematic-isotropic interface region or in the isotropic region. This motion of the glass rods in the G-R/BMAB/5CB mixture during irradiation with a UV laser is assumed to be caused by forces similar to those that cause the thermal motion of the colloidal particles in the nematic LC[6,9]. In addition, the colloidal particles in the nematic LC reportedly tend to be confined to a nematic-isotropic interface region produced by heating the mixture to the phase transition temperature for the isotropic phase and then cooling it below the clearing temperature, which produces a variety of structures depending on the cooling rate[5]. The difference in the surface tension coefficient between the particle-nematic and particle-isotropic regions of the interface and the minimization of the elastic distortion energy are thought to contribute to the confinement of the colloidal particles at the interface[5]. Therefore, if one can control the movement of the isotropic region in the nematic LC, the glass rods will be dragged through the confinement in the interface between the nematic and isotropic phases. Thus, we utilized a scanning UV laser beam to drag the glass rods by moving the nematic-isotropic interface region. However, the scanning of the UV laser beam caused only an expansion of the isotropic region as shown in Fig. 3A (Supplementary Movie 1). Consequently, the glass rods were not dragged due to a lack of translational movement of the interface by the scanning UV laser beam. The induced isotropic region maintained the isotropic phase even after the beam passed through because the *cis* form of the BMAB produced in the 5CB was stable for at least minutes (Supplementary Fig. S5A).
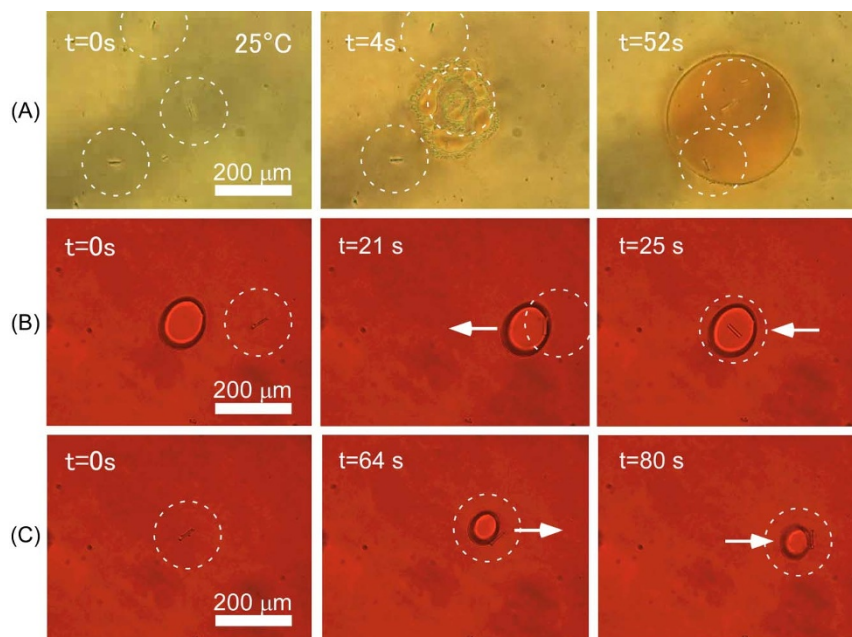
Figure 3 | Optical micrographs of the G-R/BMAB/5CB (A) and G-R/DR1/5CB (B, C) mixtures in the 50-μm glass cell obtained without a polarizer. (A) Irradiation with a UV laser (375 nm, 13 mW) at 25°C, (B) irradiation with an Ar$^+$ laser (488 nm, 15 mW) at 30°C, (C) irradiation with an Ar$^+$ laser (488 nm, 5 mW) at 30°C. The term t in figures indicates the video recording time.

Discussion

If the stability of the *cis*-BMAB in 5CB prevents dragging of the rods, the destabilization of the *cis* form will enable us to trap and freely drag small objects. Therefore, we next explored the effect of the visible light irradiation on the motion of the glass rods in the G-R/DR1/5CB mixture. The sample injected into the 50-μm homogeneous glass cell was placed on an optical microscope, and the Ar$^+$ laser was focused on the backside of the sample at 30°C. The diameter of the beam was approximately 100 μm. Irradiation at an intensity of 15 mW produced a region containing the isotropic phase, indicating that the photochemical phase transition occurred from the nematic phase to the isotopic phase at the irradiation temperature. The isotropic phase was confirmed using a polarized optical microscope. By moving the beam close to a selected glass rod, the glass rod was trapped in the beam spot or at the interface between the nematic and isotropic phases and could be dragged by moving the beam from right to center (Fig. 3B, Supplementary Fig. S5B and Movie 2). However, no manipulation was achieved by moving thermally induced isotropic region. The interface between the nematic and isotropic phases, which was induced thermally by irradiation with intense laser beam on the 5CB/NK-1951 mixture, was broadened compared to that induced photochemically with DR1. Consequently, disappearance of the isotropic region was dull, when the laser beam was scanned. The result indicates that the feature of interface is one of important contributors to the manipulation of small objects.

In addition to being dragged, a selected glass rod could be pushed by irradiating the DR1/5CB mixture with the Ar$^+$ laser at a beam intensity of 5 mW (Fig. 3C and Supplementary Movie 3), although irradiation at a 15-mW beam intensity allowed only the dragging of the glass rod. Rotational motion was also achieved as shown in Fig. 4A (Supplementary Movie 4). Polarized microscopy revealed that a laser spot size of 5 mW, which was smaller than that of the 15-mW laser beam due to technical conditions, did not exhibit the isotropic phase, although a change in the molecular orientation did occur. Whether caused by forces associated with the topological defects[9] and/or the dynamical diffusion of the LC and DR1 molecules due to the *trans–cis–trans* isomerization cycle of DR1, the size of the disordered area may contribute to this phenomenon, although the pushing mechanism remains unclear (Supplementary Figs. S6 and S7). The glass rods were also assembled by pushing and dragging them with the Ar$^+$ laser beam at 30°C (Fig. 4B). In addition, other small objects, such as polystyrene spheres and small pieces of mica, could be manipulated in the 5CB to achieve not only the motion of a single object but also the collective motion of the small objects. As shown in Fig. 5 and Supplementary Movie 5, the small objects were first confined around the interface between the nematic LC and the disordered regions and were then moved in a group by shifting and reducing the laser beam size and intensity.

The results indicate that the formation and control of the interface were the primary contributors to the manipulation of the small objects in the nematic LC. Therefore, a smectic LC can also probably be utilized as a matrix for the photochemical manipulation of small objects if one can photochemically induce such an interface in the smectic LC. Thus, we finally demonstrated the manipulation of small objects in the 8CB containing DR1 at 0.1 mol%. The DR1/8CB mixture exhibited smectic and nematic phases at temperature ranging from S (34°C) to N (41°C) I in which S, N and I represent the nematic, smectic and isotropic phases, respectively. The glass rod could be dragged and pushed by moving the Ar$^+$ laser beam (15.5 mW) at 27°C as shown in Supplementary Movie 6. The polarized microscopy revealed that the irradiation caused a phase transition from the smectic phase to the nematic phase, not the isotropic phase. In the nematic LC, the small objects assembled were found to fluctuate continually throughout the manipulation because of the fluidity. Unlike the manipulation in the nematic LC, the polystyrene particles in the smectic LC could be easily assembled (Fig. 6). The rapid transformation of the irradiated region between the nematic and smectic phases during the irradiation as well as the low fluidity of the smectic phase contributed to the successful assembly. The microscopic image in Fig. 6 reveals that the quadrupolar interaction[18] is favored over the dipolar interaction. The assembled pattern was s at 27°C without external stimuli.

In summary, a reversible photochemical phase transition of the LC mixture could be efficiently induced simply by turning on and off the visible light to initiate the *trans–cis–trans* photoisomerization cycle
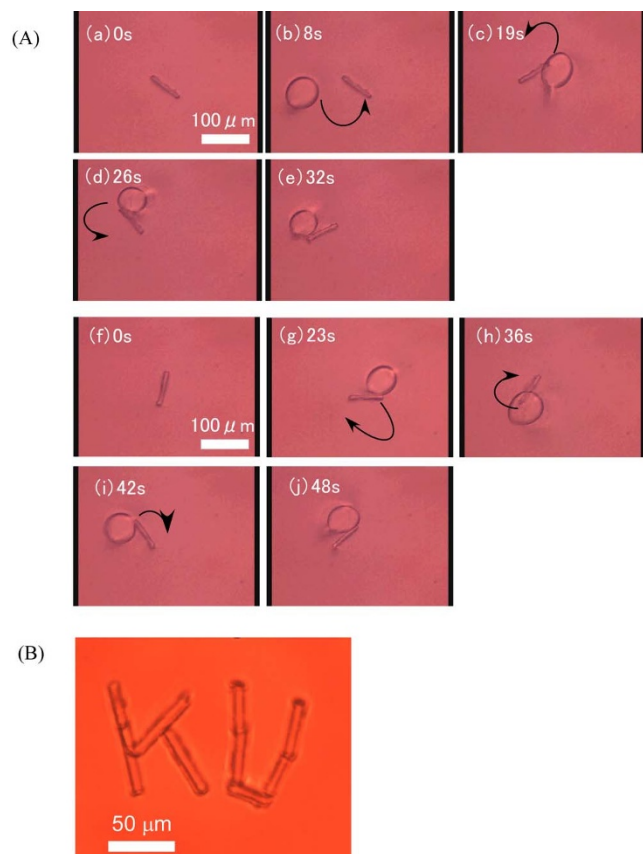
Figure 6 | **Assembly of the polystyrene spheres (ϕ = 20 µm) in the DR1/8CB mixture (0.1 mol% DR1) by moving the Ar⁺ laser beam (488 nm, 15.5 mW) at 27°C.**

Figure 4 | (A) Rotational motion of a selected glass rod (L = 30 µm, ϕ = 8 µm) in the G-R/DR1/5CB mixture (0.1 mol% DR1) by moving the Ar⁺ laser beam (488 nm, 5 mW) at 30°C: Counterclockwise rotation (a–e), clockwise rotation (f–j), and (B) assembly of the glass rods in the G-R/DR1/5CB mixture (0.1 mol% DR1) by pushing and dragging the glass rods (L = 30 µm, ϕ = 8 µm) with the Ar⁺ laser beam (488 nm, 5 mW) at 30°C.

in the DR1. The various controlled motions of the small objects—not only in the nematic LC but also in the smectic LC, such as trapping, dragging and pushing—were achieved by moving the laser beam and alte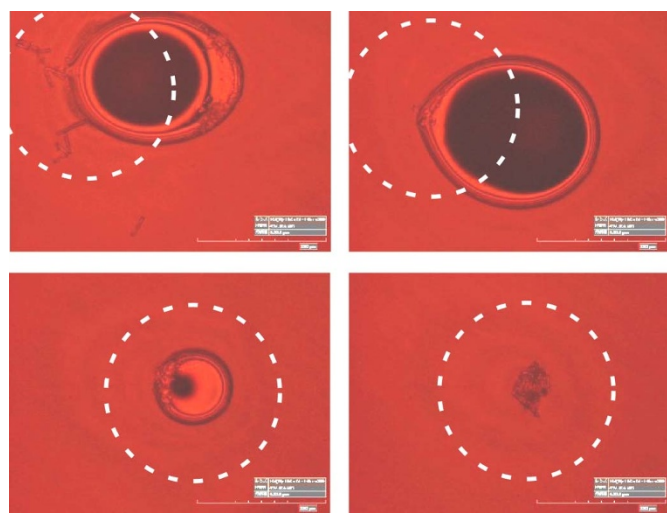ring its intensity. In previous reports, laser tweezers were used to position colloidal particles in a liquid crystal[8,10]. However, manipulation using laser tweezers generally requires much higher optical intensities with a complex optical setup. The motion of small objects in a liquid crystal presented herein is based on a dynamical change in the LC order, and, consequently, neither a complex optical setup nor increased optical laser intensity was required. The combination of the photo-controlled dynamical change in the LC order and the intrinsic self-assembly property of a liquid crystal is promising for use in technologies that require not only the organization of small objects but also the photo-driving of nano- and micro-sized mechanical materials. In addition, the reversible switching of the liquid crystallinity enables us to dynamically change the LC order, leading to a rapid reversible change in the birefringence of the LCs for use in optical devices such as displays and switchings.

Methods

The 5CB was purchase from the TCI Co. and used without further purification. Disperse Red 1 was purchased from the Aldrich Co. and was purified by recrystallization twice from ethanol. The 4-butyl-4′-methoxyazobezene (BMAB) was prepared via the diazotization of 4-n-butylaniline followed by coupling with phenol and the methylation of the phenol group. The crude solid was purified by recrystallization from ethanol. The BMAB structure was confirmed via NMR, IR and elemental analysis. The mixtures of the 5CB (or 8CB) and the dyes, BMAB and DR1, were prepared by dissolving accurately weighed mixtures (4.6 mol% BMAB in 5CB and 0.1 mol% DR1 in 5CB) in THF and evaporating the solvent. Then, the mixtures were injected into a glass cell by heating them to an isotropic phase. The thermal properties of the materials and the mixtures were examined using differential scanning calorimetry (Shimadzu DSC-60) and polarizing microscopy.

1. Poulin, P., Stark, H., Lubensky, T. C. & Weitz, D. A. Novel colloidal interactions in anisotropic fluids. *Science* **275**, 1770–1773 (1997).
2. Poulin, P., Cabuil, V. & Weitz, D. A. Direct Measurement of Colloidal Forces in an Anisotropic Solvent. *Phys. Rev. Lett.* **79**, 4862–4865 (1997).
3. Ruhwandl, R. W. & Terentjev, E. M. Long-range forces and aggregation of colloidal particles in a nematic liquid crystal. *Phys. Rev. E* **55**, 2958–2961 (1997).
4. Loudet, J. C., Barois, P. & Poulin, P. Colloidal ordering from phase separation in a liquid-crystalline continuous phase. *Nature* **407**, 611–613 (2000).
5. West, J. L., Glushchenko, A. & Liao, G. Drag on particles in a nematic suspension by a moving nematic-isotropic interface. *Phys. Rev. E* **66**, 012702–012702 (2002).
6. Musevic, I. *et al.* A. Laser trapping of small colloidal particles in a nematic liquid crystal: Clouds and ghosts. *Phys. Rev. Lett.* **93**, 187801–187801 (2004).
7. Smalyukh, I. I., Lavrentovich, O. D., Kuzmin, A. N., Kachynski, A. V. & Prasad, P. N. Elasticity-mediated self-organization and colloidal interactions of solid spheres with tangential anchoring in a nematic liquid crystal. *Phys. Rev. Lett.* **95**, 157801–157801 (2005).
8. Musevic, I., Skarabot, M., Tkalec, U., Ravnik, M. & Zumer, S. Two-Dimensional Nematic Colloidal Crystals Self-Assembled by Topological Defects. *Science* **313**, 954–958 (2006).
9. Tatarkova, S. A., Burnham, D. R., Kirby, A. K., Love, G. D. & Terentjev, E. M. Colloidal interactions and transport in nematic liquid crystals. *Phys. Rev. Lett.* **98**, 157801–157801 (2007).

Figure 5 | **Collective motion of the glass rods (L = 30 µm, ϕ = 8 µm) (a–d) and polystyrene spheres (ϕ = 8 µm) (e–h) in the G-R/DR1/5CB mixture (0.1 mol% DR1) performed by moving and reducing the beam size and intensity of the Ar⁺ laser (488 nm, 15 mW) at 30°C.**
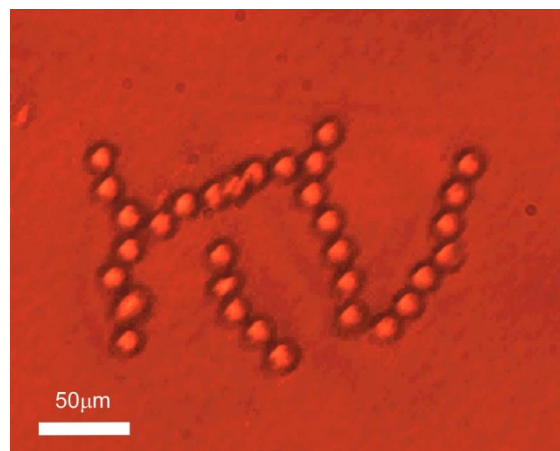
10. Yada, M., Yamamoto, J. & Yokoyama, H. Direct observation of anisotropic interparticle forces in nematic colloids with optical tweezers. *Phys. Rev. Lett.* **92**, 185501–185501 (2004).

11. Ashkin, A. Acceleration and trapping of particles by radiation pressure. *Phys. Rev. Lett.* **24**, 156–159 (1970).

12. Samitsu, S., Takanishi, Y. & Yamamoto, J. Molecular manipulator driven by spatial variation of liquid-crystalline order. *Nat. Mater.* **9**, 816–820 (2010).

13. Natansohn, A. & Rochon, P. Photoinduced Motions in Azo-Containing Polymers. *Chem. Rev.* **102**, 4139–4175 (2002).

14. Poprawa-Smoluch, M. *et al.* Photoisomerization of Disperse Red 1 studied with transient absorption spectroscopy and quantum chemical calculations. *J. Phys. Chem. A* **110**, 11926–11937 (2006).

15. Dhammila Bandara, H. M. & Burdette, S. C. Photoisomerization in different classes of azobenzene. *Chem. Soc. Rev.* **41**, 1809–1825 (2012).

16. Ikeda, T., Sasaki, T. & Ichimura, K. Photochemical switching of polarization in ferroelectric liquid-crystal films. *Nature* **361**, 428–430 (1993).

17. Ikeda, T. & Tsutsumi, O. Optical switching and image storage by means of azobenzene liquid-crystal films. *Science* **268**, 1873–1875 (1995).

18. Stalk, H. Physics of colloidal dispersions in nematic liquid crystals. *Phys. Rep.* **351**, 387–474 (2001).

Acknowledgements

Author contributions

S.K. conceived the initial idea. K.O., T.O. and R.I. designed and conducted the experiments. Y.K., T.O. and S.-N.K. advised on the experiments. All authors discussed the results, wrote and commented on the manuscript at all stages.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Kurihara, S. *et al.* Manipulation and assembly of small objects in liquid crystals by dynamical disorganizing effect of push-pull-azobenzene-dye. *Sci. Rep.* **3**, 2167; DOI:10.1038/srep02167 (2013).