



RIKEN Center for Emergent Matter
1-2 Hirosawa, Wako, Saitama 351-0198, Japan
Tel: +81-48-462-1111
Fax: +81-48-467-9599
<http://www.cems.riken.jp/en/>

July 25, 2019

Dear Dr. Xiaoyan Cao, Editor

Email: em@editorialmanager.com

Journal of Visualized Experiments

Please find the enclosed manuscript of our paper entitled:

--

Title: High-contrast and fast photorheological switching of a twist-bend nematic liquid crystal

Authors: Satoshi Aya; Péter Salamon; Daniel A. Paterson; John M. D. Storey; Corrie Imrie; Fumito Araoka; Antal Jákli; Ágnes Buka

Journal: Journal of Visualized Experiments

Manuscript ID: JoVE60433

--

We would like to thank you for handling our paper. We are also grateful to the four reviewers for reviewing our manuscript and providing their invaluable comments and feedback to us. Based on your and their comments/suggestions, we have revised the manuscript significantly to address editorial and reviewers' comments, and improved the manuscript. Please find our point-by-point responses to the reviewers. All the changes made for the manuscript are summarized as follows and highlighted in the main text. We believe that all the issues raised by you and the reviewers are now clarified.

We look forward to hearing from you soon.

Yours sincerely,

Dr. Satoshi Aya and Dr. Fumito Araoka

RIKEN Center for Emergent Matter Science (CEMS)

2-1 Hirosawa, Wako, Saitama 351-0198, Japan

E-mail: satoshiaya@scut.edu.cn, fumito.araoka@riken.jp

Tel: +81-48-462-1111 (ext. 6317)

Fax: +81-48-467-9599

Point-to-Point Reply to the Reviewers

To Reviewer 1:

We would like to thank you for reviewing our manuscript and giving us positive comments. We highly appreciate your invaluable and helpful feedback to improve our manuscript. We significantly revised our manuscript as stated in the following according to your suggestions. We hope that you are satisfied with our replies and revision. Your positive decision would be very much appreciated.

1. First, I am aware this could be a problem from the submission system and an automatically generated pdf, but better quality images are required. At least in the pdf given for revision images are very blurry, the axis labels or legends indistinguishable. POM images are so distorted that one can only interpret them in the case that you are already familiar with the kind of phases presented.

-> We revised all the figures again and uploaded the newest version.

2. Point 1.2.1, information about the alignment layer thickness for the spin-coating conditions could be provided.

-> We revised the manuscript as below.

Page 4, Line 144

(Before) “1.2.1. Prepare 1 mL of AL1254 (JSR Corp.) solution, and drip 20 μ L of the solution onto the cleaned glass substrates. Then immediately spin-coat the solution at 3000 rpm at room temperature for 70 s.”

(After) “1.2.1. Prepare 1 mL of a solution for planar alignment, AL1254 (Table of Materials), and drip 20 μ L of the solution with a pipette onto the cleaned glass substrates. Then immediately spin-coat the solution at 3000 rpm at room temperature for 70 s. The typical thickness of the alignment layer is about 20 nm.”

3. Point 1.2.2: substitute "appropriate conditions" for how do you rub it and with what.

-> We revised the manuscript as below.

Page 4, Line 147

(Before) “1.2.2. Bake the film at 80 °C for 60 min to remove the solvent and at 180 °C for more than 60 min for curing. Rub the substrates in appropriate conditions to realize uniaxial alignment of LC materials.”

(After) “1.2.2. Bake the film at 80 °C for 60 min to remove the solvent and at 180 °C for more than 60 min for curing. Rub the substrates by a rayon-cloth rubbing machine with following parameters: rotation speed at 300 rpm, plate speed 20 mm/s and an impression of 0.3 mm to realize uniaxial

alignment of LC materials.”

4. 2.1 Preparation of the LC cells: maybe some description of how (cell design, how open are the cell sides, filling points, filling direction with respect to the rubbing...) the glass substrates are glued could be useful for the readers not directly belonging to the liquid crystal community.

-> We revised the manuscript as below.

Page 4, Line 152

(Before) “2.1. Glue two glass substrates coated with the alignment layer by a photo-curable resin, Norland Optical Adhesive 65 or 81, with the aid of a LED lamp with a wavelength of 365 nm (1.1 W/cm²). Adjust the thickness of the gap between two substrates in the range of 1.7-100 μ m by using micrometer-size glass particles or polyethylene naphthalate films.”

(After) “2.1. Put a glass substrate coated with the alignment layer by a photo-curable resin onto another in a face-to-face manner and ensure they are overlapped to form a cell. Put a photoreactive adhesion (Table of Materials), mixed with micrometer-size glass particles with diameter of 1.7-100 μ m, to four corners of the cell in order to adjust the gap of cell and illuminate the cell with the aid of a LED lamp with a wavelength of 365 nm (1.1 W/cm²).”

5. 4.1.2 Information about the gap size between the rheometer plates would be valuable. In any case, more detailed steps for the rheometer usage would be also valuable. Although each rheometer has its own manual, description of standard and common steps like "geometry inertia calibration", zero gap calibration, how to correctly perform the gap trimming would be useful for the researchers with no experience with a rheometer.

-> We revised the manuscript as below.

Page 4, Line 178

(Before) “4.1.2. Set the temperature of the sample chamber to a temperature above the I-N phase transition point and then uniformly sandwich the sample between the base quartz plate and a measuring plate.”

(After) “4.1.2. Set the temperature of the sample chamber to a temperature above the I-N phase transition point (>160 °C). Set a gap value for approaching the measuring plate to the base quartz plate to sandwich the sample. Typical gap value for our measurements was 100-200 μ m. Trim the excess sample (e.g. by using paper wipes) that is out of the gap when the measuring plate stops at the trimming position, which is 25 microns above the targeted gap.”

6. 4.2. I believe information about the measurements setup conditions is necessary: constant shear stress or constant shear rate value, or the setup for the oscillatory mode mentioned. Many of this data is later

confined in the caption of Figure 3. However, a detailed and clear protocol should include this information in the main text, listing goal-operational mode-conditions.

-> We revised the manuscript as below.

Page 4, Line 186

(Before) “Irradiate UV light for measuring photorheological switching of CB6OABOBu by using a high- pressure mercury vapor short arc lamp (OmniCure S2000, Excelitas Technologies, filtered at $\lambda=365$ nm, maximum 70 mW cm⁻²). The light is guided from the beneath of the sample container through the base quartz plate. Do the measurements in oscillatory mode for extracting dynamic restoring information of the material, and steady rotational mode for obtaining effective rotational viscosity.”

(After) “Irradiate UV light for measuring photorheological switching of CB6OABOBu by using a high-pressure mercury vapor short arc lamp (Table of Materials). The light is guided from the beneath of the sample container through the base quartz plate. Do the measurements in oscillatory mode for extracting dynamic restoring information of the material, and steady rotational mode for obtaining effective rotational viscosity. For the measurements in the rotational mode, applying a constant shear stress of 13 Pa to the sample to ensure that the measurement is made in the Newtonian regime.”

7. In the section of representative results, one misses a written description that does not consist only on an enumeration of figures. Regarding both sections, Representative results and Discussion, the utility and information obtained from X-ray diffraction measurements is not covered at all. One can not find almost anywhere any statement indicating that X-ray diffraction allows to prove the structural difference between the trans-rich and cis-rich crystal phases observed and thus to fully understand the behavior of the material under UV-illumination, which in the reviewers opinion, is the main reason for adding this technique in the present manuscript more focused into testing the fast photoreological switching of a novel material. Finally, one misses in the discussion some comments on the adequacy of the protocol for the proposed goal, on the critical steps in the protocol (as for example in the liquid crystal cell fabrication, or trimming in the rheometer, or ensuring uniform and controlled illumination at any point) and on limitations of the method (example: comment on why the measured viscosity is an effective viscosity).

-> We revised the Representative results and Discussion parts to address these issues. The detailed list of the revisions can be found in the Major Revision List.

8. To continue with making protocol details complete. I believe that authors should complete the Material/Equipment table with more details: Photo-DSC equipment, polarizing microscope model, X-ray diffraction equipment... etc. Also chemicals like AL1254 (JSR Corp). None of these are basic laboratory equipment like pipettes or spatulas.

-> Thank you very much for your suggestion. We added a Material/Equipment table.

To Reviewer 2:

We would like to thank you for reviewing our manuscript. We would like to thank you for reviewing our manuscript and giving us positive comments.

To Reviewer 3:

We would like to thank you for reviewing our manuscript and giving us positive comments. We highly appreciate your invaluable and helpful feedback to improve our manuscript. We significantly revised our manuscript as stated in the following according to your suggestions. We hope that you are satisfied with our replies and revision. Your positive decision would be very much appreciated.

1. While the paper has a new idea and is reasonably well written, they never mention works carried predating the discovery of the NTB phase etc. For example V. P. Panov, M. Nagaraj, J. K. Vij, A. Kohlmeier, M. G. Tamba, R. A. Lewis, and G. H. Mehl, PRL 105, 167801 (2010) observed similar stripes for a bimesogen presumably for the first time. S. P. Sithara, V. P. Panov, J. K. Vij and G. Shanker, Liquid Crystals, 44, 244 (2017) observed the very same stripes as shown by the authors for a simple bent-core system, see their Figure 2b. Of course the colours and periodicity of the stripes depends on the cell gap. Furthermore They should also cite the first important paper that provides the first comprehensive proof of the structure of the twist bend nematic phase, Borshch et al, Nature Communications, 4, 2635-2643 (2013) in which some of the authors of this manuscript are also involved. I do not know why this paper is also not cited.

-> We added some of suggested references as below.

24. Borshch, V. et al. Nematic twist-bend phase with nanoscale modulation of molecular orientation. Nature Communications. 4, 2635-2643 (2013).

25. Panov, V. P. et al. Spontaneous Periodic Deformations in Nonchiral Planar-Aligned Bimesogens with a Nematic-Nematic Transition and a Negative Elastic Constant. Physical Review Letters. 105, 167801-1-4 (2010).

2. The On and Off Times are indicated in Figure 3 but the results should be listed in a Table giving the exposure time and the intensity of the UV light and its wavelength $\lambda = 365$ nm in the Table and characteristics when the UV is shone at different temperatures.

-> We added a table, Table 1, in order to show readers the temperature dependence of switching time.

To Reviewer 4:

We would like to thank you for reviewing our manuscript. We would like to thank you for reviewing our manuscript and giving us positive comments.

List of Major Revisions

1. Page 2, Line 80

(Before) “Here, we present key observations of a light-induced crystal-liquid phase transitions...”

(After) “Here, we observed a light-induced crystal-liquid phase transition, which are characterized by means of polarizing light microscopy (POM), photo-rheometry, photo-differential scanning calorimetry (photo-DSC) and X-ray diffraction (XRD). The light-induced crystal-liquid phase transitions presents key features...”

2. Page 2, Line 88

(Before) “POM has its advantage in offering information on the spatial distribution of the orientation of LC molecules.”

(After) “POM has its advantage in offering information on the spatial distribution of the orientation of LC molecules, and was used to determine the type of liquid crystalline phases appearing in the material and study the orientation of LCs. Photo-rheometry allows us to measure the rheological properties of materials under light stimuli and can reveal the photorheological switching properties of materials. Photo-DSC is a technique to investigate thermodynamic information of materials in darkness and also under light irradiation. Lastly, XRD allows us to study microscopic structures of materials.”

3. Page 3, Line 109

(Before) “Liquid crystals (LCs) are ideal candidates for mechanically switchable systems given the large number of existing liquid crystalline and solid phases that may be tuned by molecular design to achieve self-assembled structures having a range of different length scales. For example, while the highly symmetric fluid nematic (N) phase exhibits low viscosity due to short-range spatial order, columnar or smectic phases with 1D and 2D long- range periodicities show viscoelastic behavior. Therefore, switching between smectic or columnar, and nematic, or isotropic phases, can result in high performance switchable mechanical materials (see refs. [9–15]).”

(After) “Liquid Crystals (LCs) are ideal systems with potentially large number of liquid crystalline and solid phases that can be tuned by molecular design to allow for self-assembled structures at different length scales in particular LC phases. For example, while the high-symmetry nematic LCs (NLCs) exhibit low viscosity and elasticity because of short-range spatial order, the low-symmetry columnar or smectic LCs show high viscosity and elasticity due to one and two-dimensional long-range periodicity. It is expected that, if LC materials can be switched between two phases having large differences in their viscoelastic properties, then a viscoelastic smart material with high performance might be achieved. A few examples were reported in Ref. [9-15].

”

4. Page 3, Line 138

(Before) “1.1.1. Wash glass substrates (typical size: 1 cm x 1 cm)...”

(After) “1.1.1. Cut glass substrates by a diamond-based glass cutter (Table of Materials) to small

pieces with a typical size of 1 cm x 1 cm in square and wash them...”

5. Page 4, Line 144

(Before) “1.2.1. Prepare 1 mL of AL1254 (JSR Corp.) solution, and drip 20 μ L of the solution onto the cleaned glass substrates. Then immediately spin-coat the solution at 3000 rpm at room temperature for 70 s.”

(After) “1.2.1. Prepare 1 mL of a solution for planar alignment, AL1254 (Table of Materials), and drip 20 μ L of the solution with a pipette onto the cleaned glass substrates. Then immediately spin-coat the solution at 3000 rpm at room temperature for 70 s. The typical thickness of the alignment layer is about 20 nm.”

6. Page 4, Line 147

(Before) “1.2.2. Bake the film at 80 °C for 60 min to remove the solvent and at 180 °C for more than 60 min for curing. Rub the substrates in appropriate conditions to realize uniaxial alignment of LC materials.”

(After) “1.2.2. Bake the film at 80 °C for 60 min to remove the solvent and at 180 °C for more than 60 min for curing. Rub the substrates by a rayon-cloth rubbing machine with following parameters: rotation speed at 300 rpm, plate speed 20 mm/s and an impression of 0.3 mm to realize uniaxial alignment of LC materials.”

7. Page 4, Line 152

(Before) “2.1. Glue two glass substrates coated with the alignment layer by a photo-curable resin, Norland Optical Adhesive 65 or 81, with the aid of a LED lamp with a wavelength of 365 nm (1.1 W/cm²). Adjust the thickness of the gap between two substrates in the range of 1.7-100 μ m by using micrometer-size glass particles or polyethylene naphthalate films.”

(After) “2.1. Put a glass substrate coated with the alignment layer by a photo-curable resin onto another in a face-to-face manner and ensure they are overlapped to form a cell. Put a photoreactive adhesion (Table of Materials), mixed with micrometer-size glass particles with diameter of 1.7-100 μ m, to four corners of the cell in order to adjust the gap of cell and illuminate the cell with the aid of a LED lamp with a wavelength of 365 nm (1.1 W/cm²).”

8. Page 4, Line 158

(Before) “... , abbreviated as CB6OABOBu, at a temperature above the isotropic liquid (I)-nematic (N) phase transition into empty cells by using spatula.”

(After) “... , abbreviated as CB6OABOBu, from one of the four faces of the cell at a temperature above the isotropic liquid (I)-nematic (N) phase transition (typically at 160 °C) into empty cells by using spatula.”

9. Page 4, Line 175

(Before) “Prepare 50-150 mg CB6OABOBu powder sample, in accordance to the diameter of a measuring plate you use and load it onto the base quartz plate of a commercial rheometer (MCR 502, Anton Paar).”

(After) “Before putting the sample onto the stage of the rheometer, perform geometry inertia calibration and zero gap calibration to ensure the accuracy of the rheological study. Prepare 50-150 mg CB6OABOBu powder sample, in accordance to the diameter of a measuring plate used and load it onto the base quartz plate of a commercial rheometer, MCR 502 (Table of Materials). For the present study, a plate with a diameter of 50 mm was used.”

10. Page 4, Line 178

(Before) “4.1.2. Set the temperature of the sample chamber to a temperature above the I-N phase transition point and then uniformly sandwich the sample between the base quartz plate and a measuring plate.”

(After) “4.1.2. Set the temperature of the sample chamber to a temperature above the I-N phase transition point ($>160\text{ }^{\circ}\text{C}$). Set a gap value for approaching the measuring plate to the base quartz plate to sandwich the sample. Typical gap value for our measurements was 100-200 μm . Trim the excess sample (e.g. by using paper wipes) that is out of the gap when the measuring plate stops at the trimming position, which is 25 microns above the targeted gap.”

11. Page 4, Line 186

(Before) “Irradiate UV light for measuring photorheological switching of CB6OABOBu by using a high- pressure mercury vapor short arc lamp (OmniCure S2000, Excelitas Technologies, filtered at $\lambda=365\text{ nm}$, maximum 70 mW cm^{-2}). The light is guided from the beneath of the sample container through the base quartz plate. Do the measurements in oscillatory mode for extracting dynamic restoring information of the material, and steady rotational mode for obtaining effective rotational viscosity.”

(After) “Irradiate UV light for measuring photorheological switching of CB6OABOBu by using a high-pressure mercury vapor short arc lamp (Table of Materials). The light is guided from the beneath of the sample container through the base quartz plate. Do the measurements in oscillatory mode for extracting dynamic restoring information of the material, and steady rotational mode for obtaining effective rotational viscosity. For the measurements in the rotational mode, applying a constant shear stress of 13 Pa to the sample to ensure that the measurement is made in the Newtonian regime.”

12. Page 5, Line 211

(Newly-added sentence) “The current study was conducted in RIKEN beamline BL45XU.”

13. Page 5, Line 217

(Before) “Figure 1a,b represent the structure of CB6OABOBu and its possible conformations.”

(After) “Figure 1a,b represent the structure of CB6OABOB with its phase sequence and its possible conformations optimized by the MM2 force field in ChemBio3D.”

14. Page 5, Line 220

(Newly-added sentence) “Though the current conformational optimization made by ChemBio3D is useful for determining the conformation of a single molecule, but cannot be used for simulating conformational state of multiple molecules that are interacting or even self-assemblies of larger molecular clusters.”

15. Page 5, Line 223

(Before) “Decreasing the temperature to the TB in dark, the texture striped pattern forms, where the stripes run parallel to the rubbing direction of the LC cell (Fig. 1c, middle).”

(After) “Decreasing the temperature to the TB in dark, a striped pattern forms, where the stripes run parallel to the rubbing direction of the LC cell (Fig. 1c, middle). This stripe pattern arises as a result of buckling instability and is recognized a symbol of the TB phase, first reported in detail by Panov et al.²⁵”

16. Page 5, Line 232

(Before) “Figure 2 shows the effective viscosity of CB6OABOBu in various conditions. Figure 2a shows the temperature dependence of the effective shear viscosity.”

(After) “Figure 2 shows the effective viscosity of CB6OABOBu in various conditions measured by the rheometer. Figure 2a shows the temperature dependence of the effective shear viscosity. The reason for calling the measured viscosity the effective shear viscosity is that the real components of viscosity in liquid crystals is orientation-dependent and the measured viscosity is an orientation-averaged one in the current study.”

17. Page 6, Line 245

(Newly-added sentence) “It can be seen that the intensity at each peak changes drastically when UV light is irradiated, mainly attributed to the crystalline structural transformation and local melting.”

18. Page 7, Line 297

(Before) “At the I-N phase transition, shear-thinning is observed due to shear-induced flow alignment and the director adopts a small angle with respect to the flow direction. In the N phase, the viscosity is practically independent of the shear stress, indicating a Newtonian fluid behavior (Fig. 2b). At the transition to the TB phase, the effective shear viscosity, η_{eff} increases by an order of magnitude. This increase may be attributed to the formation of pseudo-layer structures, corresponding to the nanometer-scale heliconical director modulations. In the TB phase, strong shear thinning is observed with clear threshold values as a result of the realignment of the pseudo-

layer structures (Fig. 2b). Subsequent solidification of the sample (TB-Cr transition) is accompanied by a sharp, five orders of magnitude jump in η_{eff} . We note here that the large scattering seen in the shear viscosity data in the crystal phase is due to the large resistance of the sample exerted on the rotating cone. In this regime the sample is actually not a fluid characterized by a viscosity, but rather is a solid characterized by a storage modulus. The temperature dependencies of the apparent viscosities of samples under illumination with light of intensities 32.7 and 59.6 mW/cm² UV are also shown in Figure 2a by black filled circles and blue open diamonds, respectively. We observe three main differences between these data and those measured in darkness: 1) a reduction in the crystallization temperatures by 4 and 7 °C for 32.7 and 59.6 mW/cm² light intensities, respectively; 2) a small decrease in η_{eff} in the N phase; and 3) the disappearance of the viscosity jump at the N-TB transition for both illuminated samples. This latter observation may be explained simply by the disappearance of the TB phase, which is driven by the variation in molecular geometry from a trans-rich state to a cis-rich state.”

(After) “At the I-N phase transition, the effective viscosity, η_{eff} , decreases, which is attributed to a shear-induced flow alignment. In the N phase, the viscosity is practically independent of the shear stress, indicating a Newtonian fluid behavior (Fig. 2b). Transitioning to the TB phase results in an increase of the effective shear viscosity by an order of magnitude. Considering the TB phase has a local nematic ordering but exhibits pseudo-layer structure in an analogy with the smectic ordering, the increase of the effective shear viscosity is attributed to the formation of the pseudo-layer structures. In the TB phase, strong shear thinning is observed with clear threshold values as a result of the realignment of the pseudo-layer structures (Fig. 2b). Subsequent solidification of the sample results in a sharp jump in η_{eff} (\propto shear stress if shear rate is kept constant) by 5 orders of magnitude. The large scattering of the data of the shear viscosity in the crystal phase is a result of a large resistance of the sample exerted on the rotating cone. The sample, in this regime, is a solid characterized by a storage modulus instead of a fluid characterized by a viscosity. Results under UV intensities of 32.7 and 59.6 mW/cm² are shown by black filled circles and blue open diamonds. We observe three main differences between these data and those measured in darkness: 1) a downshift of transition temperatures; 2) decrease in η_{eff} in each phase; and 3) no significant viscosity variation about the original N-TB transition temperature for illuminated samples, which is explained by the disappearance of the TB phase under UV light.”

19. Page 7, Line 324

(Newly-added sentence) “The ON and OFF switching times are also very short (~100 s, ON and OFF switching times shown in Table 1) both at the TB and the Cr phases. The switching time is defined as the transient time for the variation of the effective viscosity from 90% to 10% of its original value (the one before UV irradiation). Since the contrast in different phases is different, the switching time cannot be fairly compared in different phases.”

20. Page 8, Line 342

(Before) “The coexistence of different crystalline structures consisting of distinct photo responsive stereoisomers in a single-component material is rare and there have been only few reports describing the photo liquefaction of crystals induced by photo switchable stereoisomers[25,26].”

(After) “So far, most of the explored photo liquefactions owe their origins to the photo-induced temperature shift of glass transition. In contrast to those, our work demonstrates a novel working mechanism in realizing fast photo liquefactions process except some recent discoveries^{27,28}.”

21. We revised the style of all the references.

22. We added two tables: Table 1 and Materials/Equipment table.