

Journal of Visualized Experiments

High-Contrast and Fast Photorheological Switching of a Twist-Bend Nematic Liquid Crystal --Manuscript Draft--

Article Type:	Invited Methods Article - JoVE Produced Video
Manuscript Number:	JoVE60433R2
Full Title:	High-Contrast and Fast Photorheological Switching of a Twist-Bend Nematic Liquid Crystal
Section/Category:	JoVE Chemistry
Keywords:	Liquid crystal, Twist-bend nematic phase, azobenzene, photo-rheology, solidification-liquefaction switching, polarized light microscopy, photo-differential scanning calorimetry, x-ray diffraction
Corresponding Author:	Satoshi Aya South China University of Technology GUANGZHOU SHI, GUANGDONG SHENG CHINA
Corresponding Author's Institution:	South China University of Technology
Corresponding Author E-Mail:	satoshiaya@scut.edu.cn
Order of Authors:	Satoshi Aya Péter Salamon Daniel A. Paterson John M. D. Storey Corrie Imrie Fumito Araoka Antal Jákli Ágnes Buka
Additional Information:	
Question	Response
Please indicate whether this article will be Standard Access or Open Access.	Standard Access (US\$2,400)
Please indicate the city, state/province, and country where this article will be filmed . Please do not use abbreviations.	Budapest, Hungary

TITLE:

High-Contrast and Fast Photorheological Switching of a Twist-Bend Nematic Liquid Crystal

AUTHORS AND AFFILIATIONS:

Satoshi Aya^{1,#}, Péter Salamon², Daniel A. Paterson³, John M. D. Storey³, Corrie Imrie³, Fumito Araoka¹, Antal Jákli⁴, Ágnes Buka²

¹RIKEN Center for Emergent Matter Science (CEMS), Wako, Saitama, Japan

²Institute for Solid State Physics and Optics, Wigner Research Center for Physics, Hungarian Academy of Sciences, Budapest, Hungary

³Department of Chemistry, School of Natural and Computing Sciences, University of Aberdeen, Aberdeen, United Kingdom

⁴Chemical Physics Interdisciplinary Program and Liquid Crystal Institute, Kent State University, Kent, OH, USA

[#]Current address: South China University of Technology, Guangzhou, China

Corresponding Authors:

Satoshi Aya (satoshi.aya@riken.jp; satoshiaya@scut.edu.cn)

Fumito Araoka (fumito.araoka@riken.jp)

Email Addresses of Co-authors:

Péter Salamon (salamon.peter@wigner.mta.hu)

Daniel A. Paterson (d.a.paterson.09@aberdeen.ac.uk)

John M. D. Storey (j.storey@abdn.ac.uk)

Corrie Imrie (c.t.imrie@abdn.ac.uk)

Antal Jákli (ajakli@kent.edu)

Ágnes Buka (buka.agnes@wigner.mta.hu)

KEYWORDS:

liquid crystal, twist-bend nematic phase, azobenzene, photo-rheology, solidification-liquefaction switching, polarized light microscopy, photo-differential scanning calorimetry, X-ray diffraction

SUMMARY:

This protocol demonstrates the preparation of a photorheological material that exhibits a solid phase, various liquid crystalline phases, and an isotropic liquid phase by increasing temperature. Presented here are methods for measuring the structure-viscoelasticity relationship of the material.

ABSTRACT:

Smart viscoelastic materials that respond to specific stimuli are one of the most attractive classes of materials important to future technologies, such as on-demand switchable adhesion technologies, actuators, molecular clutches, and nano-/microscopic mass transporters. Recently it was found that through a special solid-liquid transition, rheological properties can exhibit significant changes, thus providing suitable smart viscoelastic materials. However, designing materials with such a property is complex, and forward and backward switching times are usually long. Therefore, it is important to explore new working

mechanisms to realize solid-liquid transitions, shorten the switching time, and enhance the contrast of rheological properties during switching. Here, a light-induced crystal-liquid phase transition is observed, which is characterized by means of polarizing light microscopy (POM), photorheometry, photo-differential scanning calorimetry (photo-DSC), and X-ray diffraction (XRD). The light-induced crystal-liquid phase transition presents key features such as (1) fast switching of crystal-liquid phases for both forward and backward reactions and (2) a high contrast ratio of viscoelasticity. In the characterization, POM is advantageous in offering information on the spatial distribution of LC molecule orientations, determining the type of liquid crystalline phases appearing in the material, and studying the orientation of LCs. Photorheometry allows measurement of a material's rheological properties 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 under light irradiation. Lastly, XRD allows studying of microscopic structures of materials. The goal of this article is to clearly present how to prepare and measure the discussed properties of a photorheological material.

INTRODUCTION:

Smart mechanical materials with the capability to change their viscoelastic properties in response to environmental variation have generated tremendous interest among researchers. Switchability is considered to be the most important material factor, which offers robustness of repetitive mechanical response in living organisms. To date, artificial switchable materials with versatile functions have been designed by utilizing soft matter (i.e., photoresponsive hydrogels¹⁻³, polymers⁴⁻¹¹, liquid crystals [LCs]⁹⁻¹⁷, pH-responsive micelles¹⁸⁻²², and surfactants²³). However, these materials suffer from more than one of the following problems: lack of reversibility, low switching contrast ratio of viscoelasticity, low adaptivity, and slow switching speed. In conventional materials, a tradeoff exists between the switching contrast ratio of viscoelasticity and switching speed; thus, designing materials covering all of these criteria with high performance is challenging. To realize materials with the aforementioned omnicapability, selecting or designing molecules that carry emergent natures of both high fluidity (viscous property) and rigidity (elastic property) is essential.

Liquid crystals are ideal systems with a potentially large number of liquid crystalline and solid phases that can be tuned by molecular design. This allows for self-assembled structures at different length scales in particular LC phases. For example, while high-symmetry nematic LCs (NLCs) exhibit low viscosity and elasticity because of their short-range spatial order, low-symmetry columnar or smectic LCs show high viscosity and elasticity due to one- and two-dimensional long-range periodicities. It is expected that if LC materials can be switched between two phases with large differences in their viscoelastic properties, then a viscoelastic smart material with high performance can be achieved. A few examples have been reported⁹⁻¹⁵.

This article demonstrates the preparation of a photorheological LC material with a phase sequence of isotropic (I)-nematic (N)-twist-bend nematic (TB)²⁴-crystal (Cry) upon cooling (and vice versa upon heating), which exhibits fast and reversible viscoelastic switching in response to light. Presented here are the methods for measuring viscoelasticity and an illustration of the microscopic structure-viscoelasticity relationship. Details are described in the representative results and discussion sections.

95
96 **PROTOCOL:**

97
98 **1. Preparation of rubbed surfaces for aligning LC molecules planarly**

99
100 1.1. Prepare clean glass substrates.

101
102 1.1.1. Cut glass substrates using a diamond-based glass cutter (**Table of Materials**) into small
103 square pieces with averages sizes of 1 cm x 1 cm. Wash them by sonication at 38 kHz or 42
104 kHz in an alkaline detergent (**Table of Materials**, diluted in water at a detergent:water volume
105 ratio of 1:3) and rinse with distilled water repeatedly (typically, more than 10x with 5 min of
106 sonication for each rinse).

107
108 1.1.2. Subject the substrates to ultraviolet-ozone (UV-O₃) cleaner (**Table of Materials**) for
109 more than 10 min.

110
111 1.2. Coat planar alignment layer onto clean glass substrates.

112
113 1.2.1. Drip 20 µL of 1 mL of a polyimide planar alignment solution (**Table of Materials**, used
114 as is) with a pipette onto the cleaned glass substrates. Immediately spin-coat the solution,
115 using a spin coater (**Table of Materials**) at 3,000 rpm and room temperature (RT) for 70 s.

116
117 NOTE: The typical thickness of the alignment layer is about 20 nm.

118
119 1.2.2. Bake the coated glass substrates at 80 °C for 60 min to remove the solvent and at 180
120 °C for >60 min for curing. Rub the substrates using a rayon-cloth rubbing machine (**Table of**
121 **Materials**) with the following parameters: rotation speed = 300 rpm, plate speed = 20 mm/s,
122 and impression = 0.3 mm to realize uniaxial alignment of LC materials.

123
124 **2. Preparation of LC cells**

125
126 2.1. Place a glass substrate coated with the alignment layer onto another substrate, with the
127 alignment layers face-to-face, and ensure that they are 80% overlapped to form a cell.

128
129 NOTE: The 20% nonoverlapped surfaces are to be used for introducing LC materials into the
130 cell.

131
132 2.2. Place 100 µL of a photoreactive adhesive (**Table of Materials**) and 0.1 mg of micrometer-
133 sized glass particles (diameter = 5 µm) onto a clean glass substrate and mix them manually
134 using the tip of a paper clip. Move the mixed material to four corners of the cell to adjust the
135 cell gap and illuminate the cell using a low-pressure mercury vapor short arc lamp (**Table of**
136 **Materials**) with a wavelength of 365 nm (1.1 W/cm²). Place the cell under the LED lamp at a
137 distance of 1 cm for 5 min.

138
139 2.3. After illumination, place the cell onto a hot stage and set the target temperature of the
140 stage to heat the cell to a temperature above the isotropic liquid (I)-nematic (N) phase
141 transition (typically at 160 °C). Transfer the LC material (1-[4-butoxyazobenzene-4'-yloxy]-6-

[4-cyanobiphenyl-4' yl]hexane; CB6OABOBu; 0.2–10.0 μ L) onto one open surface of the cell and push the materials towards the cell entrance using a microspatula to obtain contact between the LC material and entrance of the cell. Wait for the LC materials to be filled in the cell by capillary force.

NOTE: CB6OABOBu has a phase sequence: Cry 100.3 $^{\circ}$ C TB 105.2 $^{\circ}$ C N 151.7 $^{\circ}$ C I on heating and I 151.4 $^{\circ}$ C N 104.5 $^{\circ}$ C TB 83 $^{\circ}$ C Cry on cooling. Do not introduce CB6OABOBu into the N phase or TB phase because flow-induced alignment is promoted.

3. Texture characterization by polarizing optical microscopy

3.1. Observe the LC cells placed on the hot stage to control the sample temperature (40–180 $^{\circ}$ C) with ± 0.1 K accuracy under a polarizing light microscope (POM, **Table of Materials**) using 4x–100x objective lenses. Record textures using a digital color camera sequentially during cooling and heating.

3.2. Use a UV epi-illuminator (**Table of Materials**) equipped on the POM with a wavelength of 365 nm (50 mW/cm²).

4. Photorheological measurements

4.1. Prepare of rheological measurements.

4.1.1. Before placing any sample onto the stage of the rheometer (**Table of Materials**), perform geometry inertia calibration and zero gap calibration controlled by a software according to manufacturer's instructions to ensure accuracy of the rheological study. Weigh 250 mg of the CB6OABOBu powder sample and load it onto the base quartz plate of the rheometer.

NOTE: For the present study, a plate with a diameter of 50 mm is used.

4.1.2. Set the temperature of the sample chamber to a value above the I-N phase transition point (>160 $^{\circ}$ C). Set a gap value for approaching the measuring plate to the base quartz plate to sandwich the sample (typical gap value used = 20 μ m). Trim excess sample (e.g., by using paper wipes) that is outside of the gap when the measuring plate stops at the trimming position, which is 25 μ m above the targeted gap.

NOTE: Do not allow excess amount of CB6OABOBu to be introduced to the sample chamber, as this makes the measurements inaccurate.

4.2. Perform rheological measurements.

4.2.1. Irradiate UV light at 365 nm (1–100 mW/cm²), measuring photorheological switching of CB6OABOBu using the high-pressure mercury vapor short arc lamp.

NOTE: The light will be guided from beneath the sample container through the base quartz plate.

4.2.2. Perform measurements in 1) oscillatory mode for extracting dynamic restoring information of the material and 2) steady rotational mode for obtaining effective rotational viscosity. For measurements in rotational mode, apply a constant shear stress of 13 Pa to the sample to ensure that the measurement is made in the Newtonian regime.

NOTE: The selection of the modes is performed by a software according to the manufacturer's instructions.

5. Photo-differential scanning calorimetry

5.1. Weigh 10 mg of CB6OABOBu powder sample and load it into a gold differential scanning calorimetry (DSC) pan. Heat the sample to 170 °C in the isotropic phase and ensure that there is no inhomogeneous sample distribution in the DSC pan as observed by the naked eye. Cover the DSC pan with a quartz plate.

5.2. Perform photo-DSC measurements according to the manufacturer's instructions (**Table of Materials**). Measure DSC data at a scan of 10 °C/min.

NOTE: The photo-DSC machine is equipped with a UV light intensity of 50 mW/cm².

6. X-ray diffraction characterization

6.1. Heat the powder CB6OABOBu sample using the hot stage at 170 °C and suck the sample into an XRD capillary (diameter = 0.5 mm) by capillary force.

6.2. Attach the capillary to a sample holder equipped with a temperature controller. Set the chamber temperature (60 °C, 70 °C, 80 °C, 90 °C, 100 °C, 110 °C, 120 °C, 130 °C, 140 °C, 150 °C, 160 °C, and 170 °C for each X-ray diffraction measurement).

6.3. Irradiate the sample by X-ray and detect the diffracted X-ray beams by a detector without UV irradiation and under a UV light intensity of 10 mW/cm² for 1 min and 10 min.

NOTE: The current study was conducted in RIKEN beamline BL45XU. The light source was the SPring-8 standard in-vacuum undulator. A liquid nitrogen-cooled Si double crystal monochromator was used to monochromatize the beam. The wavelength was 1 Å.

REPRESENTATIVE RESULTS:

POM images, photorheometric data, photo-DSC data, and XRD intensity profiles were collected in darkness during temperature variation and while shining UV light. **Figure 1a,b** represents the structure of CB6OABOBu, with its phase sequence and possible conformations optimized by the MM2 forcefield in the modeling program (e.g., ChemBio3D).

When CB6OABOBu is in the trans-state, two energy-plausible conformational states appear, and the twisted conformation is the most stable one that promotes formation of the TB phase. When CB6OABOBu is excited to the cis-state when exposed to UV light, a kink-conformation is realized. Though the current conformational optimization made by the

modeling program is useful for determining the conformation of a single molecule, it cannot be used for simulating conformational state of multiple molecules that are interacting, or even for self-assemblies of larger molecular clusters.

Figure 1c,d shows the POM textures in darkness and under 30 mW cm^{-2} UV irradiance, during cooling of the sample in a $2 \text{ }\mu\text{m}$ -thick LC cell with uniformly rubbed planar alignment. In the N phase, uniaxial alignment of molecules is realized (**Figure 1c**, top). When decreasing the temperature to the TB in darkness, a striped pattern forms, at which the stripes run parallel to the rubbing direction of the LC cell (**Figure 1c**, middle). This stripe pattern arises as a result of buckling instability and is recognized as a symbol of the TB phase, first reported by Panov et al.²⁵. Further decreasing of the temperature leads to crystallization (**Figure 1c**, bottom). Irradiation of the UV light alters conformation from the trans- to cis-state, resulting in phase variation and thus texture variation. If starting from the TB phase, the UV light transforms the striped texture to the uniaxially aligned state of the N phase (**Figure 1d**, top-middle). Turning off the UV light allows the molecules to relax and reenter the trans-state, and the striped texture of the TB phase forms again.

Figure 2 shows the effective viscosity of CB6OABOBu under 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 are orientation-dependent, and the measured viscosity is an orientation-averaged value in the current study. **Figure 2b** shows the shear stress dependence of the effective shear viscosity at different temperatures during the first and second runs. **Figure 2c** presents variation among the effective shear viscosity triggered by UV irradiation at different temperatures. **Figure 2d** demonstrates switching curves of the effective shear viscosity in a log scale at two different temperatures, (i.e., one in the N phase and the other in the TB phase). The detailed temperature dependence of the switching times is summarized in **Table 1**.

Figure 3a,b shows the textures of CB6OABOBu in a nonaligned sample under 50 mW/cm^2 UV irradiance at $80 \text{ }^\circ\text{C}$ (**Figure 3a**) and after cooling to $60 \text{ }^\circ\text{C}$ (**Figure 3b**). Photo-DSC curves of **Figure 3c** demonstrate that upon cooling, I-N phase transitions of the trans- and cis-isomers are different. Though the photo-DSC is useful for detecting differences between the dark- and light-stimulated states, it should be noted that photo-DSC usually makes it difficult to quantitatively compare the real heat flow of the differences, since the baseline of the DSC curves changes significantly due to light absorption by the sample and the metal surface of the DSC pan. **Figure 3d** demonstrates that upon heating, the melting of the crystal phase of the trans- and cis-isomers are different, as measured by conventional DSC. **Figure 3e,f** shows XRD diffraction plots of the diffracted intensity as a function of d-spacing without and with UV irradiation, respectively. 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.

FIGURE AND TABLE LEGENDS:

Figure 1: Chemical structure of CB6OABOBu and the evolution of textures on cooling. (a) Chemical structure of CB6OABOBu and its phase sequence. (b) Space-filling molecular models

of CB6OABOBu optimized by the MM2 forcefield in the modeling program. (c) POM textures of CB6OABOBu under crossed polarizers in a 2 μm -thick cell with uniformly rubbed planar alignment; during cooling without UV illumination. Top: in the N phase at 140 $^{\circ}\text{C}$; middle: in the TB phase at 104 $^{\circ}\text{C}$; bottom: at the TB-Cry phase transition. (d) POM textures at 90 $^{\circ}\text{C}$ illustrating the photoswitching process. Top: before UV; middle: coexistence of N and TB phases shortly after 30 mW/cm^2 UV irradiance at 365 nm; bottom: relaxed TB texture after switching off the UV illumination. Scale bars represent 100 μm . This figure has been adapted with permission from Aya et al.²⁶.

Figure 2: Rheological properties and photodynamics of photoswitching of the rheological properties of CB6OABOBu. (a) Temperature dependence of the effective shear viscosity measured at a constant shear stress of 13 Pa in rotational mode with different UV irradiances: 0 mW/cm^2 (red circles), 32.7 mW/cm^2 (black circles), and 59.6 mW/cm^2 (blue diamonds). (b) The effective shear viscosity as a function of increasing shear stress at selected temperatures. Black filled circles (100 $^{\circ}\text{C}$) and green filled diamonds (102 $^{\circ}\text{C}$) are data measured on the first scan, while black open circles (100 $^{\circ}\text{C}$) and green open diamonds (102 $^{\circ}\text{C}$) are the data measured on the second scan. (c) Repeatable photoswitching of the effective shear viscosity at 59.6 mW/cm^2 irradiance. High and low values in each temperature correspond to UV-OFF and UV-ON states. (d) Photoswitching of the effective shear viscosity shown on a log scale at 97 $^{\circ}\text{C}$ in the TB phase and 90 $^{\circ}\text{C}$ in the Cry phase. Blue and red solid lines for the TB phase are best-fitting curves using simple exponential function upon UV-ON and UV-OFF states. The UV intensity is 59.6 mW/cm^2 . This figure has been modified and adapted with permission from Aya et al.²⁶.

Figure 3: Evidence of existence of micro-segregated domains with different crystal structures in the Cry phase. (a,b) POM textures through blue filter under 50 mW/cm^2 UV irradiance in an octagonal spot of the shape of the field iris diaphragm in the middle at (a) 80 $^{\circ}\text{C}$ and (b) 60 $^{\circ}\text{C}$. (c) Temperature dependences of the heat flow of the sample during cooling at a rate of 10 $^{\circ}\text{C}/\text{min}$ without UV (black dots) and under UV (blue dots). (d) Temperature dependences of the heat flow of the trans-rich sample during heating at 2 $^{\circ}\text{C}/\text{min}$ and 10 $^{\circ}\text{C}/\text{min}$ rates (black and blue curves, respectively) without UV, and of the cis-rich sample at 2 $^{\circ}\text{C}/\text{min}$ rate (red curve). (e,f) Shown is d-spacing dependence of the wide angle X-ray diffraction intensity. (f) Magnified view of the small d-value region of panel e. Blue dashed, red solid, and black long-dashed lines indicate the X-ray diffraction profiles without UV illumination, under 10 mW/cm^2 irradiance for 1 min and 10 min, respectively. Open upward and filled downward triangles show increases and decreases in the diffracted intensity of each peak. This figure has been modified and adapted with permission from Aya et al.²⁶.

DISCUSSION:

As revealed in **Figure 1**, CB6OABOBu is a photo-responsive material with I, N, TB, and Cry phase sequences upon cooling. Since local ordering of these phases differs significantly, the photo-driven switching of rheological properties is expected to exhibit good viscoelastic contrast. To quantitatively investigate this, photo-rheology measurements were performed.

First, we consider the rheological data measured in the dark (**Figure 2a**, red open circles). 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 (**Figure 2b**). Transitioning to the TB phase results in an increase of the effective shear viscosity by one order of magnitude. Considering that the TB phase has a local nematic ordering but exhibits pseudo-layer structure analogous to the smectic ordering, the increase of the effective shear viscosity is attributed to formation of the pseudo-layer structures.

In the TB phase, strong shear thinning is observed with clear threshold values as a result of realignment of the pseudo-layer structures (**Figure 2b**). Subsequent solidification of the sample results in a sharp jump in η_{eff} (\propto shear stress if shear rate is kept constant) by five orders of magnitude. The large scattering of the shear viscosity data in the crystal phase is a result of the sample's large resistance exerted on the rotating cone. The sample, in this regime, is a solid characterized by storage modulus instead of a fluid characterized by viscosity. Results under UV intensities of 32.7 mW/cm² and 59.6 mW/cm² are shown as black filled circles and blue open diamonds. Three main differences are observed between this data and that measured in darkness: 1) a downshift of transition temperatures, 2) a decrease in η_{eff} in each phase, and 3) no significant viscosity variation among the original N-TB transition temperature for illuminated samples, which is explained by the disappearance of the TB phase under UV light.

It is clear that the rheological properties are indeed significantly distinct in different phases. To test the photo-driven rheological switching, rheological measurements were performed by shining UV light onto the sample. **Figure 2c** reveals that the photo-driven rheological switching has different contrast values at different temperatures: nearly 1 in the I and N phases, 10 in the TB phase, and 10⁶ in the Cry phase. The ON and OFF switching times are also very short (\sim 100 s, ON and OFF switching times shown in **Table 1**) both in the TB and Cry phases. The switching time is defined as the transient time for the variation of effective viscosity from 90% to 10% of its original value (that before the UV irradiation). Since the contrast in different phases is different, the switching time cannot be fairly compared between different phases. It is worth noting that for other molten liquids, the initial crystal phase typically recovers within several hours to several days, since their high viscosity prevents backward reaction in bulk, even at high temperatures^{9,14}.

To determine the reason for the absence of slow nucleation, POM observation, photo-DSC, and XRD measurements were conducted. As the POM images in **Figure 3** show, shining UV in the Cry phase triggers melting to the I phase at 80 °C (cis-state rich). Maintaining the UV irradiation while decreasing the temperature causes crystallization of the cis-state molecules to occur at different temperatures than those of the trans-state. This suggests a microsegregation of trans- and cis-states. Photo-DSC data give direct evidence for this. As **Figure 3c,d** shows, exposure to UV light results in splitting of the phase transition peaks for both the I-N (on cooling) and crystal melting (on heating). These confirm that trans- and cis-state molecules form different phase structures. Thus far, most of the explored photo liquefactions owe their origins to the photo-induced temperature shift of glass transition. In contrast, this work demonstrates a novel working mechanism in realizing fast photo liquefaction processes, except for some recent discoveries^{27,28}.

ACKNOWLEDGMENTS:

This work was supported by the HAS-JSPS bilateral joint research project. Financial support

from grants NKFIH PD 121019 and FK 125134 is acknowledged.

DISCLOSURES:

The authors have nothing to disclose.

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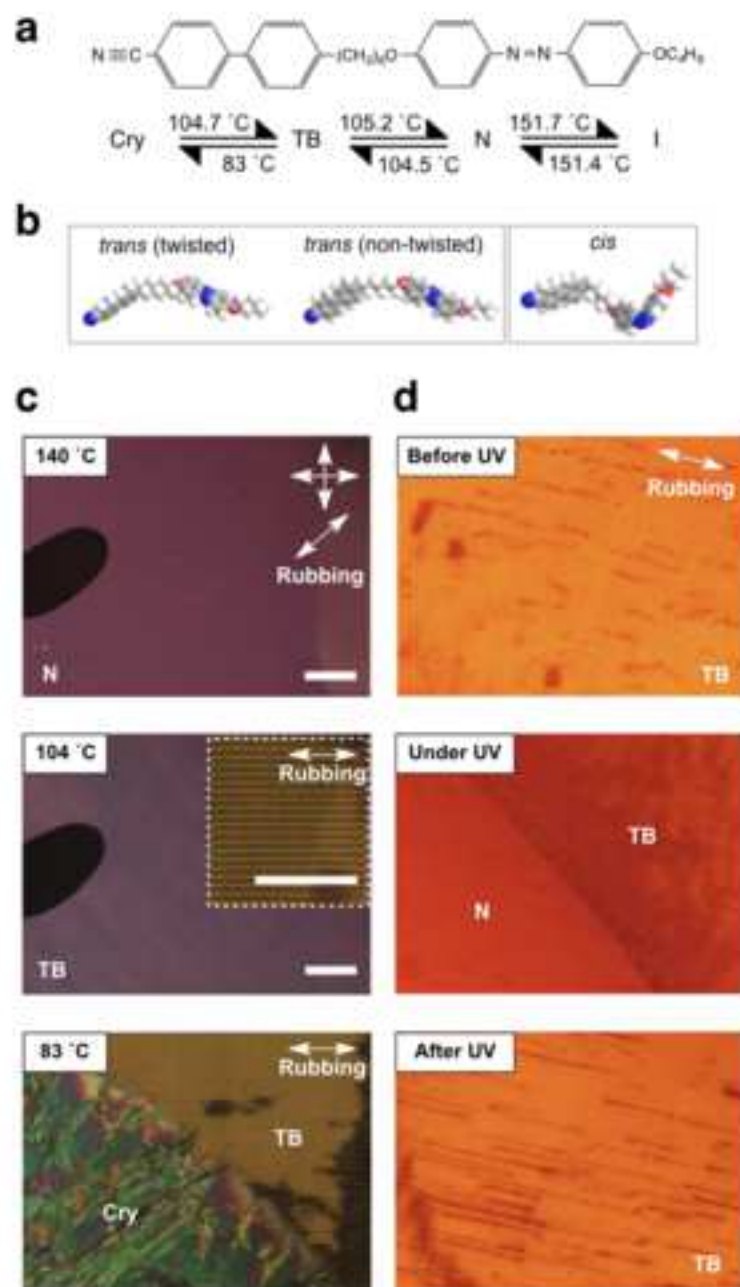
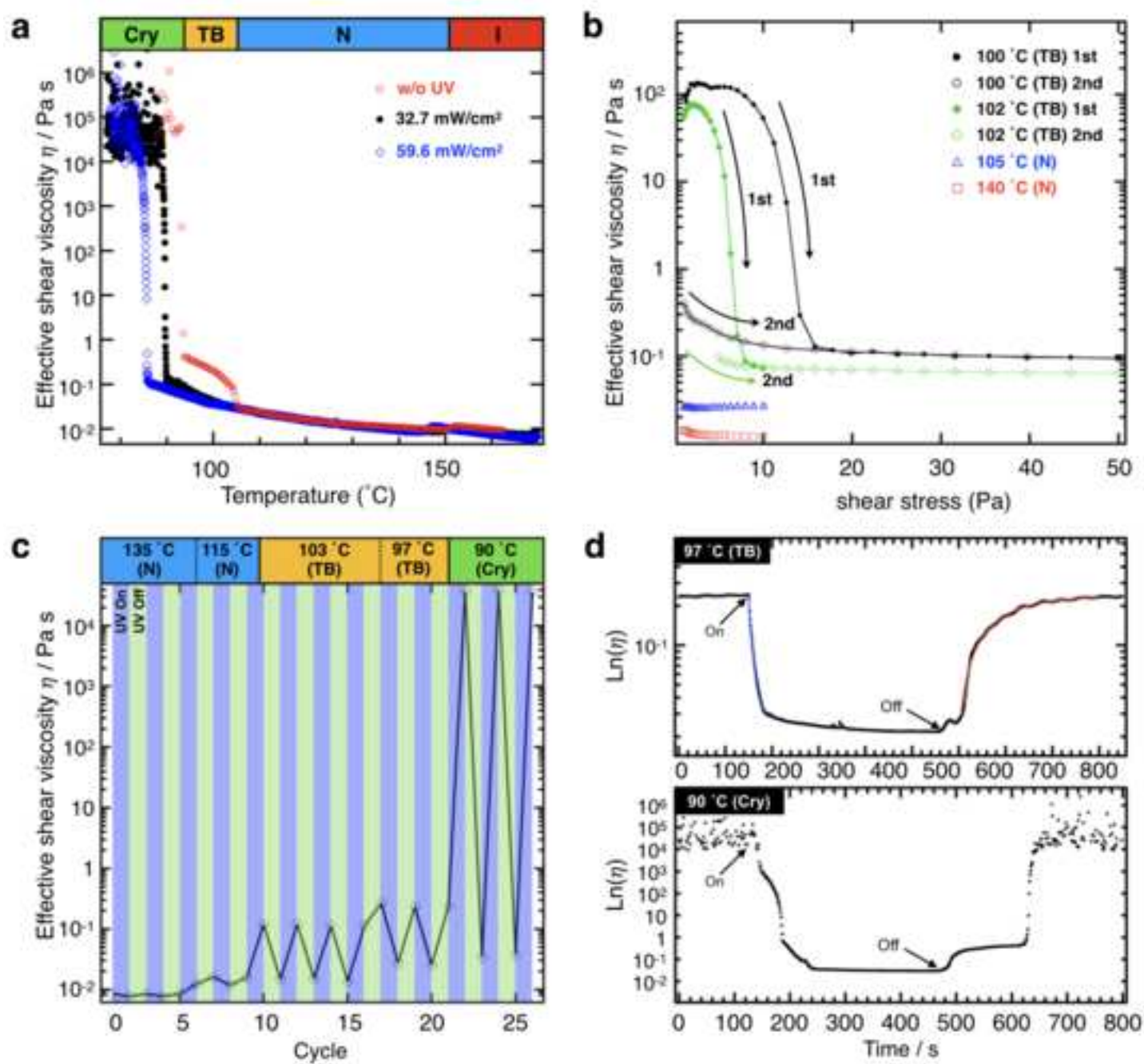
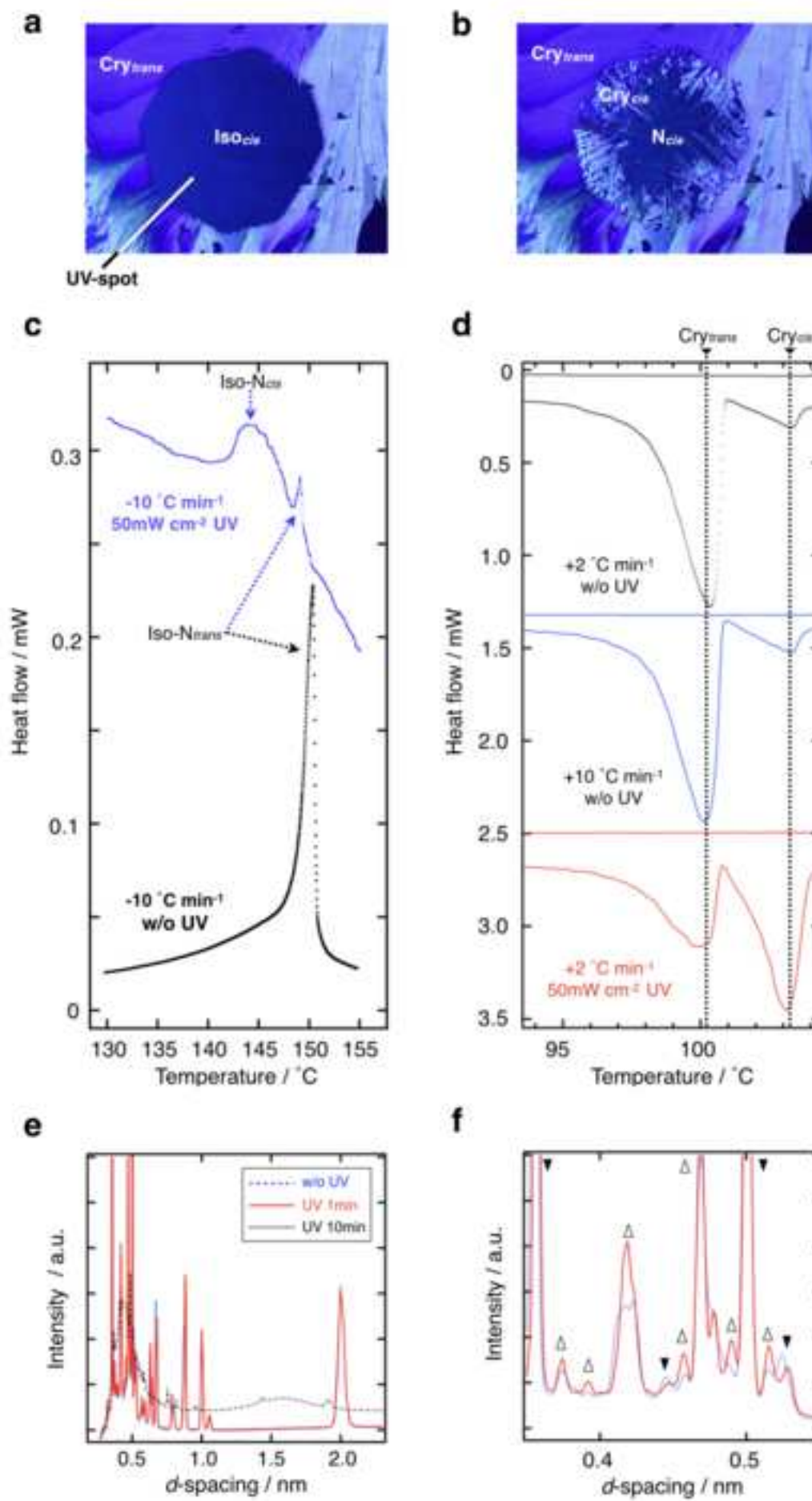


Figure 2

[Click here to access/download;Figure;Figure2.tiff](#)



Phase	Temperature (°C)	ON switching rate (s)	Off switching rate (s)
Isotropic	155	119	126
Nematic	135	116	170
Nematic	115	130	238
Twist-bend nematic	103	14	126
Twist-bend nematic	102	14	138
Twist-bend nematic	97	16	212
Crystal	90	73	35
Crystal	89	78	38

Name of Material/ Equipment	Company	Catalog Number
21-401-10	AS ONE	
AL1254	JSR	
BX53P	Olympus	
Discovery DSC 25P	TI instruments	
Glass cutter PRO-1A	Sankyo	
HS82	Mettler Toledo	
MCR502	Anton Paar	
MRJ-100S	EHC	
Norland Optical Adhesive 65, 81	Norland Products	
OmniCure S2000	Excelitas Technologies	
PILATUS 6M	Dectris	
S1126	Matsunami Glass	
SC-158H	EHC	
SCAT-20X	DKS	
SLUV-4	AS ONE	
UV-208	Technovision	

Comments/Description

Microspatula

Planar alignment agent for liquid crystals

Polarising microscope with transmission/epi-illumination units

Photo-DSC equipment

A diamond-based glass cutter

hot stage

A commercial rheometer

Rubbing machine

Photoreactive adhesions

A commercial high-pressure mercury vapor short arc lamp. Maximum 70 mW/cm².

Hybrid photon counting detector for X-ray diffraction detection

Glass substrate

Spin coater

Alkaline detergent

Low-pressure mercury vapor short arc lamp

Ultraviolet-ozone (UV-O3) cleaner



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Title of Article:

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

Author(s):

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

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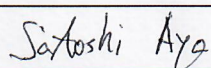
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CORRESPONDING AUTHOR

Name:	Satoshi Aya	
Department:	Center for Emergent Matter Science (CEMS)	
Institution:	RIKEN	
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RIKEN Center for Emergent Matter
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Tel: +81-48-462-1111
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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].”

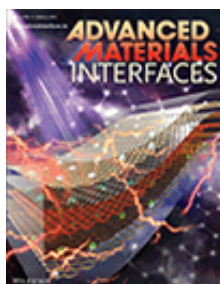
(After) “So far, most of the explored photo liquefactions owe their origins to the photo-induced temperature shift of glass transition. In contrast to those, our work demonstrates a novel working mechanism in realizing fast photo liquefactions process except some recent discoveries^{27,28}.”

21. We revised the style of all the references.

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



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Title: Fast-and-Giant Photorheological Effect in a Liquid Crystal Dimer

Author: Satoshi Aya, Péter Salamon, Daniel A. Paterson, et al

Publication: Advanced Materials Interfaces

Publisher: John Wiley and Sons

Date: Apr 8, 2019

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Licensed Content Author	Satoshi Aya, Péter Salamon, Daniel A. Paterson, et al
Licensed Content Date	Apr 8, 2019
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Title of new article	High-contrast and fast viscoelastic photoswitching of a twist-bend nematic liquid crystal
Publication the new article is in	Journal of Visualized Experiments
Publisher of new article	MyJove Corp
Author of new article	Satoshi Aya, Péter Salamon, Daniel A. Paterson, John M. D. Storey, Corrie T. Imrie, Fumito Araoka, Antal Jákli, Ágnes Buka

Expected publication date of new article	Jul 2019
Estimated size of new article (pages)	7
Requestor Location	SATOSHI AYA 2-1 Hirosawa Wako, Saitama 351-0198 Japan Attn: SATOSHI AYA
Publisher Tax ID	EU826007151
Total	0 JPY

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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/>

August 2, 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. Based on your comments/suggestions, we revised the manuscript as highlighted in the main text. Also, according the revisions we made in the main manuscript, we revised the Material/Equipment Table. We believe that all the issues raised by you 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