CHEMISTRY & BIOTECH

THE UNIVERSITY OF TOKYO
SCHOOL OF ENGINEERING

December 10, 2018

Dear Dr. Vineeta Bajaj
Science Editor, Journal of Visualized Experiments

Attached please find the manuscript of our paper entitled

MS No. JoVE59244
(New title) Electrochemical Cholesteric Liquid Crystalline Device for Quick and Low-Voltage Color Modulation
(Old title) Cholesteric Liquid Crystalline Display Device for Quick and Low-Voltage Color Modulation Enabled by Redox-Responsive Chiral Dopant

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by Shoichi Tokunaga, Mengyan Zeng, Yoshimitsu Itoh*, Fumito Araoka, Takuzo Aida

Thank you very much for your kind e-mail of November 27, 2018, concerning our above manuscript. We are pleased to know that all the reviewers feel that our manuscript deserves publication after appropriate revisions. As attached, we revised the manuscript properly. Please also find in the following [1] Summary of Revisions and [2] Point-to-Point Answers to Editorial and Reviewers' Comments. We uploaded the revised manuscript and Supporting Information with revised parts marked with a red color. We now believe that the revised version is ready for publication. We look forward to your final decision as soon as possible.

Thank you very much once again.
With best regards,

Yoshimitsu Itoh

[1] Summary of Revisions for Quick Understanding of the Editor

1. The title was changed.
2. The experimental protocol that should be filmed was highlighted in yellow.
3. Some of the description was moved from "Discussion" to "Representative Results" with minor modifications (lines 201–225).
4. A new text regarding the color modulation range (lines 251–261) and the color modulation speed (lines 272–280) was added to "Discussion".
5. A minor grammatical corrections were carried out.

[2] Point-to-Point Answers to Editorial and Reviewers' Comments

To Editor

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues.

=> We have thoroughly read and corrected any spelling or grammatical errors.

2. Please obtain explicit copyright permission to reuse any figure/table from a previous publication. Explicit permission can be expressed in the form of a letter from the editor or a link to the editorial policy that allows re-prints. Please upload this information as a .doc or .docx file to your Editorial Manager account. The Figure/Table must be cited appropriately in the Figure Legend, i.e. "This figure/table has been modified from [citation]."

=> This manuscript is based on our previous paper (*J. Am. Chem. Soc.* **2018**, *140*, 10946) and borrowed some of the figures from the paper. Therefore, we have obtained and attached the copy right permission from the publisher.

3. Please shorten the title to be more concise if possible.

=> As suggested, we would like to change the title to "Electrochemical Cholesteric Liquid Crystalline Device for Quick and Low-Voltage Color Modulation"

4. Please revise the protocol text to avoid the use of any personal pronouns (e.g., "we", "you", "our" etc.).

=> We have revised the text thoroughly.

5. Please revise the protocol to contain only action items that direct the reader to do something (e.g., "Do this," "Ensure that," etc.). The actions should be described in the imperative tense in complete sentences wherever possible. Avoid usage of phrases such as "could be," "should be," and "would be" throughout the Protocol. Any text that cannot be written in the imperative tense may be added as a "Note." Please include all safety procedures and use of hoods, etc. However, notes should be used sparingly and actions should be described in the imperative tense wherever possible. Please move the discussion about the protocol to the Discussion.

=> We have revised the text thoroughly.

6. Please add more details to your protocol steps. There should be enough detail in each step to supplement the actions seen in the video so that viewers can easily replicate the protocol. Please ensure you answer the "how" question, i.e., how is the step performed? Alternatively, add references to published material specifying how to perform the protocol action. See examples below.

   1.4: Is this step performed in a hood? Please note all safety procedures.

   => This step is performed in a well-ventilated hood. We have note all the procedures related to safety issues in the main text.

   1.5: Is a certain device used here? Please specify.

   => An oil rotary vacuum pump is used to evaporate the dichloromethane at ~ 5.0 Pa. This is now described in the revised text in lines 95–97. We also added the information of the pump in the materials list.

   2.1.1: What is used to cut the glass? Does the surface patterned with ITO have a higher resistance? Please specify.

   => A diamond tipped glass cutter is used to cut the glass. We have added the information of the glass cutter in the materials list. The ITO patterned side can be easily identified using digital multi-meter because the glass surface coated (patterned) with ITO have low resistance (resistance: ~30 Ω), while the other side has high resistance (nonconductive). The description related to the above has now been revised (lines 101–108).

   2.1.4, 2.1.5, 2.2.1: Please specify the sonication power used throughout the procedure.

   => We added the catalog number of ultrasonic bath and its power (40 W) in the materials list.

7. Please include single-line spaces between all paragraphs, headings, steps, etc.

   => We have revised the manuscript thoroughly.

8. After you have made all the recommended changes to your protocol (listed above), please highlight 2.75 pages or less of the Protocol (including headings and spacing) that identifies the essential steps of the protocol for the video, i.e., the steps that should be visualized to tell the most cohesive story of the Protocol.

9. Please highlight complete sentences (not parts of sentences). Please ensure that the highlighted part of the step includes at least one action that is written in imperative tense.
10. Please include all relevant details that are required to perform the step in the highlighting. For example: If step 2.5 is highlighted for filming and the details of how to perform the step are given in steps 2.5.1 and 2.5.2, then the sub-steps where the details are provided must be highlighted.

=> We have highlighted the necessary part for filming.

11. Please revise to explain the Representative Results in the context of the technique you have described, e.g., how do these results show the technique, suggestions about how to analyze the outcome, etc. The paragraph text should refer to all of the figures. However for figures showing the experimental set-up, please reference them in the Protocol. Please removing relevant text in the Discussion section to the Representative Results section.
    JoVE articles are focused on the methods and the protocol, thus the discussion should be similarly focused. Please revise the Discussion to explicitly cover the following in detail in 3-6 paragraphs with citations:
    a) Critical steps within the protocol
    b) Any modifications and troubleshooting of the technique
    c) Any limitations of the technique
    d) The significance with respect to existing methods
    e) Any future applications of the technique

=> In order to fulfill the editor's request, we have moved and modified some text (lines 201–225) from "Discussion" to "Representative Result". We also added a new text (lines 251–261, and 272–280) in the "Discussion" according to the request from the editor as well as from the reviewers.

13. Table of Materials: Please sort the items in alphabetical order according to the Name of Material/Equipment.

=> We have revised the table accordingly.

To Reviewer #1

In this manuscript, the authors describe the fabrication processes and the operating procedures of a cholesteric liquid crystal (CLC) display device with fast electrical response and low operating voltage. The experimental procedures are clearly written and results are also interesting. The manuscript can be accepted for publication after minor revisions. Some specific questions and comments are listed as follows:

=> We highly appreciate this positive evaluation.

1. On page 2 (line 102), please show the LC phase transition temperatures of the employed orange LC mixture. The melting point of 5OCB is 48 ºC, but the operating temperature is 37 ºC. Thus, the melting point of the employed LC mixture should be below 37 ºC, unless it is super-cooling effect.

=> The temperature range of the cholesteric phase is from 46.8 °C to 3.2 °C on cooling and from 4.8 °C to 49.7 °C on heating confirmed by differential scanning calorimetry (DSC) measurement (scan rate: 5 °C/min). This is now described in the revised text in lines 201–203.

2. On page 5 (line 232), the bandwidth Δλ is calculated based on the ordinary and extraordinary refractive indices of 5OCB at the corresponding central wavelength (467 nm). What are the n_o and n_e values at this wavelength?

=> We do not have the exact n_o and n_e values of 5OCB at 467 nm. The approximate refractive indices of 5OCB that we employed to calculate the bandwidth was measured at 589 nm (ref. 32).

3. The reflection color of CLC devices is sensitive to the view angle. What is the viewing angle?

=> The viewing angle is 0 ° (perpendicular to the LC device) and the incident angle is also 0° upon transmittance measurement. This is now described in the revised text in lines 182–183.

4. Please explain why the transmittance at 510 nm keeps decreasing, as shown in Fig. 2C. The transmittance change results from the HTP change of the redox-responsive chiral dopant, the degradation shows whether the HTP change would not be reversible.

=> The reason why the transmittance keeps decreasing is due to the orientational disorder of the LC material not due to the degradation of the chiral dopant. In fact, when the device is applied with a shear force by pushing the center of the glass cell, the device recovers its initial orientational LC order and the transmittance. This is described in the main text in lines 215–217.

5. On page 5 (lines 239 and 240), the 467 nm and 485 nm should be exchanged. In addition, the wavelength of 485 nm is not a green wavelength.

=> Thank you very much for your comments. We have corrected the description of the wavelength. Regarding the color description, the definition is rather ambiguous. We simply described the color as "green" that matched our intuitive color recognition.

6. Please reformat your references.

=> We have checked and corrected the references so that they match with the designated format of this journal.

To Reviewer #2

Using cholesteric liquid crystal made of the nematic 5OCB and the redox-responsive chiral dopant ^{Fc}**D**, the authors demonstrate a novel design concept of tunable Bragg's reflection color achieved by redox reactions. The suggested display device is characterized by its low operation voltage and fast response. This research accomplishment has been orally reported in ILCC 2018, Kyoto, in July and a paper has been published in *J. Am. Chem. Soc.*, August 2, 2018 (Web). In this work, the authors describe the procedure of material and sample preparations and experimental measurements in detail to allow the reader to easily reproduce the experiment. The reviewer believes that the manuscript can be accepted after the authors properly address the following points:

=> We highly appreciate this positive evaluation.

1. It is clear that this work is closely related to Ref. 19 authored by the same Japanese research group (S. Tokunaga, Y. Itoh, H. Tanaka, F. Araoka, and T. Aida, "A redox-responsive chiral dopant for quick electrochemical color modulation of cholesteric liquid crystal," DOI: 10.1021/jacs.8b06323). Two figures out of three in this manuscript are identical to those appearing in Ref. 19. They should be specifically modified or properly credited to avoid self-plagiarisms. Please make sure no duplicated text should exist in this work.

=> We have obtained a copyright permission from the publisher to reuse the figure and appropriately described it in the figure caption. We also confirm that there is not text duplication.

2. Line 134-137: Please provide useful information on the temperature and humidity conditions for coating. Also, what are the times for hard and soft baking after spin-coating $PEDOT^{+}$?

=> The spin coating procedure was carried out at ambient conditions (~25 °C, humidity: ~45%). Then the sample was kept under the ambient conditions for 1 h without baking, according to the procedure in ref. 35. This is now described in the revised text in lines 131–134.

3. Generally, a CLC exhibits the Grandjean (planar) texture as the most (optically) stable state when a planar or homogeneously aligned cell is used. In this work, what if an aligning agent is introduced to impose the desired planar alignment? Please comment on the structural stability and level of defects of the planar texture with a vertical helix after an electrically induced redox reaction.

=> As described in lines 138–140, we were able to obtain a well-aligned planar orientation simply by rubbing the ITO patterned glass plate. In this device, the exposure of the LC mixture to the ITO electrode is necessary to induce the efficient electrochemical reaction of $^{Fc}\mathbf{D}$. Therefore, it is not appropriate to use an aligning agent for this device. Regarding the LC orientation after the redox reactions, it gradually degrades when we repeat the redox cycle. The degraded orientation can be completely recovered simply by applying a shear force (pushing the glass surface of the device). This is described in the revised text in lines 215–217.

4. In the experiment, a 1.5-V voltage drives the center wavelength of Bragg's reflection band to shift from 467 nm to 485 nm, by a redshift of 18 nm only. How does the voltage amplitude govern the (amount of the) shift? It would be useful to provide a plot of the shift as a function of the voltage amplitude.

=> The reason for small band shift is due to a reverse reaction (reduction of $^{Fc}\mathbf{D}^+$) taking place at the interface of LC mixture and PEDOT film (Fig. 1C). Therefore, the reflection color will be determined by the ratio between $^{Fc}\mathbf{D}$ and $^{Fc}\mathbf{D}^+$ in the LC mixture. This is now described in the revised text in lines 248–253.

=> When we took a cyclic voltammogram (CV) of $^{Fc}\mathbf{D}$, its half-wave potential appears at +0.61 V and irreversible peak appears at +2.2 V. Therefore, the appropriate driving voltage should be between +0.61 and +2.2 V. In fact, when we applied a higher voltage (*e.g.* +2.5 V), the color shift was more significant (623 nm, orange) but not reversible. This is now described in the revised text in lines 257–260.

5. Based on Figure 2(D), the reviewer is suspicious of the authors' claim that the rise time is 2.7 s. At what maximum transmittance (at 510 nm) do the authors consider it the 100% value to determine the rise time? How do the rise time and fall time vary at a different wavelength, say, in blue?

=> After switching the voltage to 0 V, the transmittance at 510 nm leveled off after 8 s. Therefore, we have employed the value at this time as the 100% value to the rise time. The difference between the forward and backward color modulation speed is still not clear at this moment. One possibility is the applied potential relative to the half-wave potential of the device ($E_{1/2}$ = +0.61 V); For the forward and backward reaction, the applied voltage is 0.89 V above and 0.61 V below the $E_{1/2}$, respectively. The larger difference could induce faster change. The other possibility is the occurrence of a reverse reaction taking place at the interface of LC mixture and PEDOT film (Fig. 1C), which gives rather complicated reaction mechanism for the backward change.

6. Line 350: "28" is mistaken as "29."

=> We have revised the text.

To Reviewer #3

The authors present the realization of display component with the use of chiral nematic crystal. The method of fabrication is clearly presented and the work is interesting for a broad audience.

=> We highly appreciate this positive evaluation.

1 One suggestion that I have is that the Authors could more highlight the fast speed modulation and the low operating voltage by presenting on text some relevant values from the state of the art. Also a comment of the different response of the on-to-off state to the off-to-on state would be interesting. Which value is compared with the current technology?

=> The color modulation speed of our device is by far the fastest and lowest in the operation voltage among related examples. We have added a text (lines 272–278) describing this discussion. The response speed that we emphasize is the forward color modulation. The difference between the forward and backward color modulation speed is still not clear at this moment. One possibility is the applied potential relative to the half-wave potential of the device ($E_{1/2}$ = +0.61 V); For the forward and backward reaction, the applied voltage is 0.89 V above and 0.61 V below the $E_{1/2}$, respectively. The larger difference could induce faster change. The other possibility is the occurrence of a reverse reaction taking place at the interface of LC mixture and PEDOT film (Fig. 1C), which gives rather complicated reaction mechanism for the backward change.