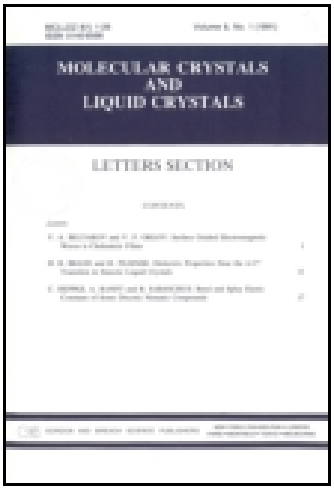

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

High Sensitive and Selective Virus Based Structural Colorimetric Sensor

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Published online: 17 Nov 2014.

To cite this article: Chuntae Kim, So-Young Lee, Won-Guen Kim & Jin-Woo Oh (2014) High Sensitive and Selective Virus Based Structural Colorimetric Sensor, Molecular Crystals and Liquid Crystals, 598:1, 171-175, DOI: 10.1080/15421406.2014.933389

To link to this article: http://dx.doi.org/10.1080/15421406.2014.933389

Mol. Cryst. Liq. Cryst., Vol. 598: pp. 171–175, 2014

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.933389

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High Sensitive and Selective Virus Based Structural Colorimetric Sensor

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Inspired by natural colorization, we developed a virus (M13KE bacteriophage) based innovative colorimetric sensor which can detect various kinds of chemicals or contaminant materials. Using M13KE bacteriophage, we self-assembled responsive color matrices composed of quasi-ordered fiber bundle structures. Changes in the fiber bundle structures in response to stimuli led to changes in the color of the matrices. For example, upon exposure to volatile organic solvents (VOCs), the multi-colored matrices exhibited distinct solvent polarity-dependent color changes that could be recognized by the naked eye. Our innovative colorimetric sensors can be useful for many kinds of harmful toxic molecules and pathogens detections to improve national security and public welfare.

Keywords Virus; M13KE bacteriophage; colorimetric sensor; volatile organic solvents

1. Introduction

In the nature, some living things can change their colors to express their mood and communicate each other or avoid enemies [1–3]. Inspired by natural colorization, many researchers have investigated biomimetic color sensors, which can be responded with various target molecules. Although many man-made nanomaterials have been demonstrated to recapitulate intricate biophotonic structures for novel biosensor applications [4–8], tailoring their specific functions to respond customized targets is still challenging. Current methods to promote selectivity require chemical incorporation of recognition motifs or the synthesis of an array of chemically modified, cross-responsive photonic structures for "artificial nose" type pattern recognition [7, 9]. These techniques are promising but far more difficult to implement because they require the design and synthetic incorporation of recognition motifs.

Here, we developed a virus (M13KE bacteriophage) based innovative colorimetric sensor which can detect various kinds of chemicals or contaminant materials. Using virus, we fabricated self-assembled nanostructure which can generate the distinct color through

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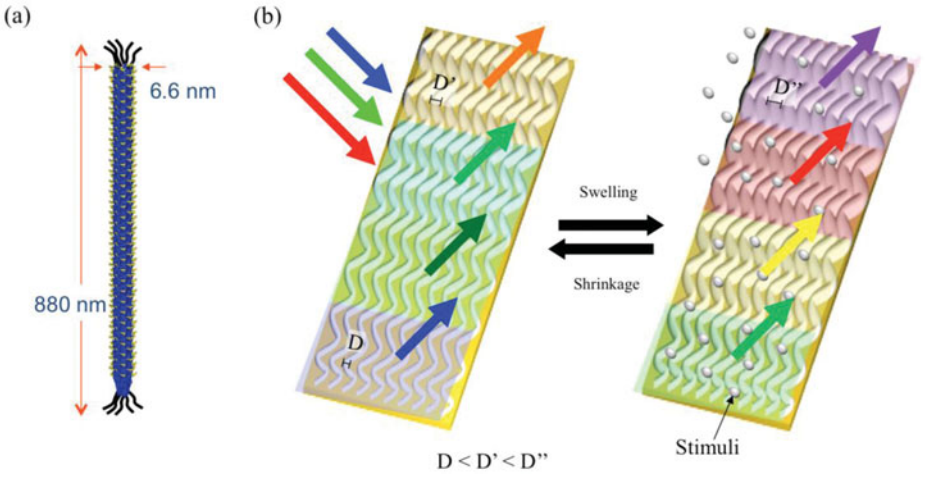

Scheme 1. Scheme for (a) M13KE bacteriophage which is used in this work and (b) principle of our virus based colorimetric sensor. Each matrix is composed of quasi-ordered fiber bundles with different diameter and interspacing, and exhibits a different color. D: diameter of bundle resulted in fast pulling speed, D': diameter of bundle resulted in slow pulling speed, D": diameter of swelled bundle.

coherent scattering (Scheme 1). Upon exposure the volatile organic compounds (VOCs), the colorimetric sensor exhibited the different color change response depended on the polarity of VOC. Our innovative colorimetric sensors can be useful for many kinds of harmful toxic molecules and pathogens detections to improve national security and public welfare.

2. Experimental Methods

Color Film Fabrication: The virus which used in this work was derived from M13KE phage (cat. #N0316S, New England Biolab) and amplified through general mass amplification protocol [10, 11]. We fabricated the virus self-assembled multiple color band patterns using the previously developed simple pulling method [12]. The colors of the assembled structures were varied by controlling the pulling speed between 20 and 80 mm/min. We constructed a home-built phage deposition apparatus by modifying a syringe pump. We programmed software using Cþþ to control the motor speed (between 0.1 μm/min and 30 mm/mim) through an RS232C cable. For preparing Phage litmus matrices, we used 6mgml^{-1} 4E phage suspensions in Tris-buffered saline (12.5 mM Tris and 37.5 mM NaCl, pH 7.5). Phage density in the resulting film is 1.9–2.9 $\times$ 10^{12} number of particles/cm^2 which was calculated by the formula as below:

Number of phages/mL =
$(6 \times 1016) * (A269 - A320)/$(number of DNA Bases in the genome of the phage)
A269: UV absorbance at 269 nm, A320: UV absorbance at 320 nm

Atomic Force Microscopy (AFM) Analysis: AFM images were collected using an MFP3D AMF (Asylum Research, Santa Barbara, CA) and analyzed using Igor Pro 6.0 (WaveMetrics, Inc. Lake Oswego, OR) and Asylum software package (Asylum Research, Santa

Barbara, CA). All images were taken using tapping mode with a tip spring constant of 2 N/m. The nanoprobe tips were made of silicon with 10 nm in radius.

VOCs Sensing System: We used the home-built sensing system which was developed for real time VOCs detection [13]. We monitored the color change of colorimetric film using the digital microscope which was attached on top of gas sensing chamber. The VOC vapors were obtained by injection of a volume solvent needed to achieve each concentration into a small container inside the chamber through inlet tube. The RGB color difference generated from VOCs detection was exhibited by a home-made MATLAB program as well.

3. Results and Discussion

Figure 1 shows the virus based multi-color matrices and their AFM images. The exhibited colors of assembled structures were varied by controlling pulling speed between 30-50 μm/min. Tuning the structure of the liquid crystalline virus film caused distinct changes in color, allowing the possible use of virus particles as versatile photonic materials. As the pulling speed increased, virus bundle diameter, their interspacing and matrix thickness which influence the observed structural colors gradually decreased and the generated color wavelength was blue-shifted from red to green and blue. Figure 1(c) shows that the observed colors are attributable to coherent scattering form the fiber bundle structure.

Figure 2 shows sensing results using our virus colorimetric film. The virus based colorimetric film exhibited characteristic color changes when exposed to target molecules. When we applied target molecule, the phage bundles in virus film were swelled and increased interspacing between fiber bundles. The changes in color were due to modulation of the phage bundle structures and subsequent thickness changes, with each band swelling to a different extent. Upon exposure to very low concentration (15 ppm) of ethanol and water, the bands of the virus based colorimetric film immediately changed color. Figure 2 shows

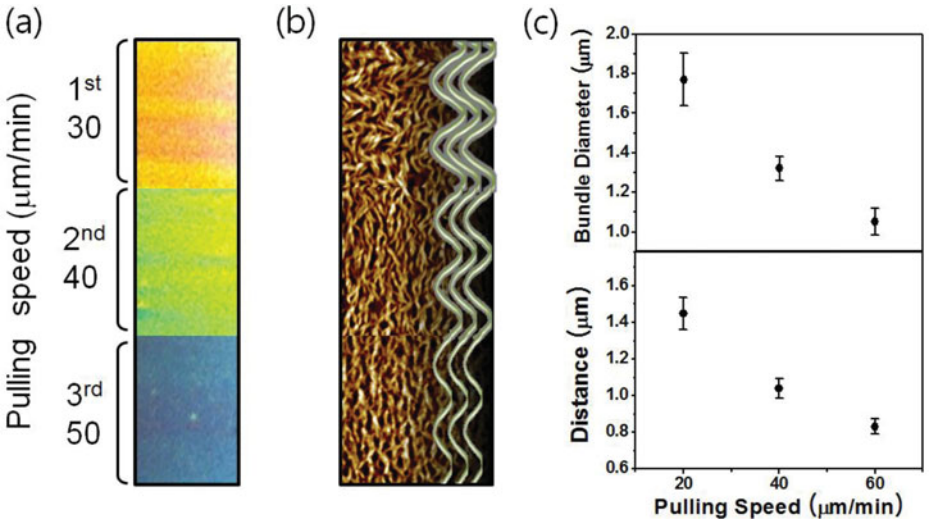

Figure 1. Fabricated virus based color matrices images (a) and their AFM images (b), respectively. (c) Modulation of phage bundle structures by different pulling speeds. The effects of different pulling speeds (30–50 μm/min) on phage bundle diameter and distance between the bundles. Analyzed data was made on at least 10 different areas of the phage matrices.

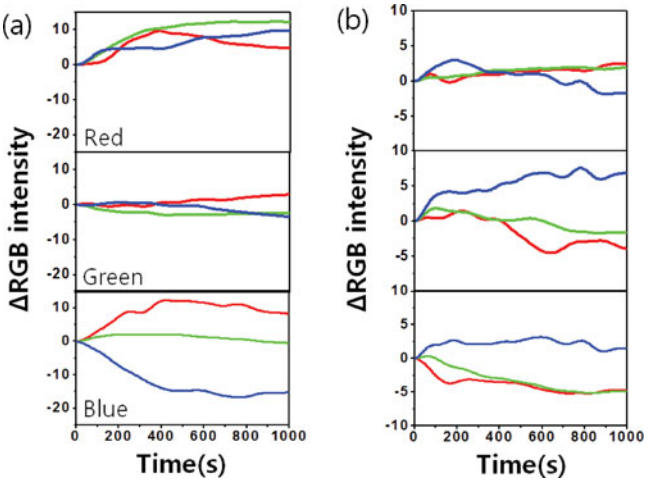

Figure 2. The time dependent of RGB color change profile of virus based colorimetric sensor exposed to 15 ppm concentration of DI-water (a) and ethanol (b). Each plot represents the ΔRGB color intensity of each color matrix.

the real time ΔRGB analysis data in each band. Quantitative real time response to DI-water and ethanol was recorded by a CCD video camera coupled with a homemade MATLAB program for RGB component analysis. As you can see in Figure 2, based on our sensing system, the virus based colorimetric film selectively distinguished and discriminated the ethanol and water in very low concentration.

4. Conclusions

Our customized virus based colorimetric sensor has multiple advantages over conventional structural color sensors. Easily fabricated multiple colorimetric matrices through a one-step self-assembly process can be simply applied to detect target molecules. Our sensitive and selective virus based colorimetric sensors promise to establish a rapid, portable, and simple but effective means of detection for various harmful chemical and biological toxins.

Acknowledgment

This work was supported by the 2012 Specialization Project Research Grant funded by the Pusan National University.

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