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A Color Display System Based on Thermochromic Conjugated Polydiacetylene Supramolecules

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Introduction

Owing to the very intriguing structural, mechanistic, and optical properties associated with the extensively conjugated ene-yne backbones, polydiacetylene (PDA) supramolecules have received enormous attention among many chemical, biochemical and material scientists.¹⁻¹⁵ A notable interesting thing is the brilliant blue-to-red color transition property that occurs upon environmental perturbations such as heat, mechanical stress, organic solvent and ligand-receptor interactions, which has been elegantly applied to the construction of a variety of sensor systems.¹⁸⁻²³

Although other applications such as field emission,²⁴ nonlinear optics²⁵ and solar cells²⁶ have been reported, the majority of the PDA applications have been the chromic-based sensors.¹⁸⁻²³ We now report preliminary results on the PDA-based multi-color display device. As components of display devices, interest in polymers is increasing due to their attractive properties. There have been a number of attempts to create a sandwich-structured display based on electrochromic polymers with a driving voltage.²⁷⁻²⁹ A 3-D electrochromic design has been reported with an array form.³⁰ It

evolved into flexible display types that are collectively composed of organic active layers and pixel-encapsulated liquid crystals.^{31,32} Furthermore, smart pixels printed on paper were successfully fabricated with electrochemically driven active matrix transistors.³³ Thermochromic displays are the candidates for chromatic devices. Recently, a novel display type fabricated from dual-color thermochromic powder and embedded wiring patterns was demonstrated.³⁴

Most of the reported studies based on conceptual and emerging display technologies have not provided a full color range for multi-purpose applications. Moreover, the fabrication process to generate the pixel patterns remains a considerable challenge. Therefore, researches have been limited to showing the feasibility of display devices with constrained centimeter-size windows.^{35,36} The present study introduces a PDA-based multi-color thermochromic display device with a micro-pixel array and reduction of the thermal interference among adjacent cells.

Experimental

A UV-sensitive amine-terminated diacetylene monomer, PCDA-EDEA (10, 12-pentacosa-diynoic acid-2-2'(ethylenedioxy) bis (ethylamine)), was obtained by reacting PCDA-NHS (*N*-hydroxysuccinimide ester of 10,12-pentacosadiynoic acid) with an excess amount of EDEA (2,2'(ethylenedioxy)diethylamine) in methylene chloride, as described in the literature.³⁷ Due to the difficulty in fabricating a uniform film of PCDA-EDEA, a diacetylene vesicle solution was mixed with an aqueous 10% PVA (polyvinyl alcohol) (Aldrich, Mw=89,000-98,000) solution at a volume ratio of 1:1. The irradiation of photosensitive monomer-PVA by 254 nm of UV-light causes a shift of the film color from opaque to blue and results in the polymer state of the composition, which is represented as PDA-PVA. After the polymerization, blue to red (at 70 °C) and red to yellow-green changes (at 180 °C) with transition tones are achieved using the thermochromic property of the film.³⁸

For a demonstration of the multi-color thermochromic display, a device composed of Pyrex glass substrate, a serpentine-type micro-heater array, a thick SU-8 layer and a PDA-PVA composite film was fabricated (Figure 1). A micro-heater was designed in a serpentine form to provide maximized thermal energy by Joule heating over a local area. The SU-8 layer plays two key roles: thermal isolation among adjacent cells and an embedded photomask without misalignment. A Pyrex glass wafer of 800 μm in thickness was used as a starting material. It was cleaned with a H₂SO₄:H₂O₂ (1:1) solution and the serpentine-type micro-heater array was then fabricated on the substrate with quadruple metal layers of Ti/Au/Ti/Au (10/50/10/200 nm). The top two Ti/Au (10/200 nm) layers of the micro-heater regions were partly etched

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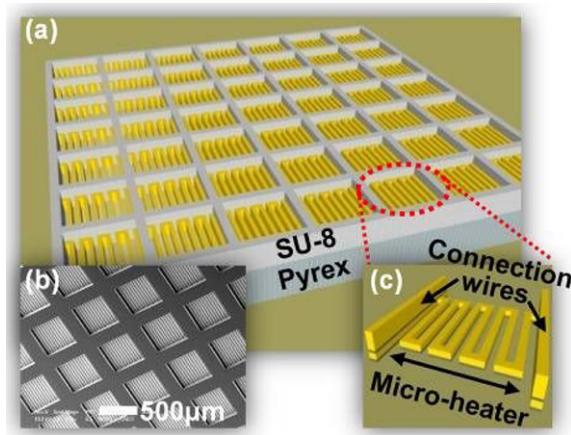


Figure 1. (a) Device schematics, (b) SEM image of device and (c) 3-D sketch of a micro-heater with connection wires.

away, leaving the connection wires, as shown in Figure 1(c). A SU-8 layer with a thickness of 100 μm was spin-coated and patterned with window size that exactly matched to that of the micro-heaters (Figures 1(a) and 1(b)). The micro-heaters were designed to be 500×500 and $700 \times 700 \mu\text{m}^2$ with spacing between adjacent windows of 200 and 100 μm , respectively.

The adhesion of the monomer-PVA film on Pyrex was improved via an oxygen plasma treatment just before the film coating on the surface with a plasma power of 150 W and a gas flow rate of 50 sccm for 5 min. A composite polymer solution of 150 μL was then dispensed on a $1 \times 2.3 \text{ cm}^2$ SU-8 patterned glass. After a curing time of 18 h, a solid film of 50 μm , which served as a thermochromic layer actuated by a proper voltage, was formed on the substrate. Finally, a polydimethylsiloxane (PDMS, Dow Corning) coating was applied as a protection layer.

Results and Discussion

Blue micro-pixel images on the film could be generated by UV irradiation with a designed external photomask and an aligner via front side exposure in a conventional manner. Nonetheless, it should be noted that the device structure itself includes a SU-8 layer that can act as an internally embedded photomask to remove any misalignment and reduce the complexity of the process. Hence, pixel generation is performed using a back side UV irradiation scheme in a self-aligned process. Using this method, the 254 nm UV light passes through the Pyrex glass but is stopped by the SU-8 layer. The transmittance values of the Pyrex glass (18%) and SU-8 (0%) layer to the 254 nm UV light are described in the literature.³⁸ In consequence, polymerization of the monomer-PVA film, corresponding to the open windows of SU-8 layer, generated blue micro-pixel patterns of identical size, whereas the film region that was protected by SU-8

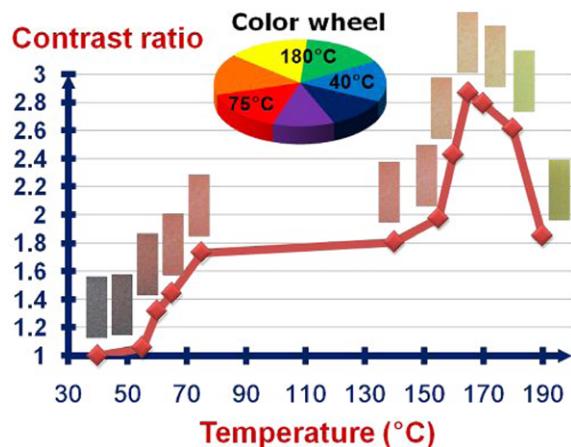


Figure 2. Contrast ratio vs. temperature characteristics of PDA-PVA film between 30 and 190 °C. The organic film was prepared on a $2 \times 3 \text{ cm}^2$ Pyrex glass substrate and the temperature-dependent film images were captured by a CCD camera.

layer remained unchanged.

To investigate the full color characteristics of the thermochromic film (i.e., a solid phase of PDA-PVA), the film was formed on a $2 \times 3 \text{ cm}^2$ glass substrate in the aforementioned dispensing and curing method. It was then irradiated with 254 nm UV-light for 10 min. For the application of heat to the film-coated substrate, it was put on a hot plate. The temperature of the film was read using a digital thermometer with a thermocouple probe directly attached to the substrate. Subsequently, temperature-dependent images were captured using a CCD camera.

The temperature-dependent CCD camera images with corresponding CR values are illustrated in Figure 2. While a blue color was observed below 40 °C, a blue-to-red transition of the film occurred between 40 and 75 °C. Full-red color with CR of 1.73 was accomplished at 75 °C. It is clear from the figure that there is no significant color change from 75 to 140 °C. The thermochromic shift continued from red to orange at 165 °C (CR=2.87) and ended with yellow-green at 180 °C. Increasing the temperature further completed the color cycle with green at 190 °C; however, eventually, became permanently damaged at temperatures in excess of 190 °C.

Micro-pixel chromism was investigated with respect to various applied potentials and switching times. Figures 3(b)-3(d) show CCD camera captured images of $700 \times 700 \mu\text{m}^2$ pixel array of which the middle rows were activated with 4, 5 and 6 V, respectively.

The switching time of the array was kept short enough not to disturb the adjacent inactive pixels. By inspecting the color chart shown in Figure 2, the temperature of the active pixels can be estimated to be less than 40 °C in the off state; and 55, 60 and 65 °C at 4, 5 and 6 V, respectively. Figures 3(e)-3(h) show a $500 \times 500 \mu\text{m}^2$ pixel array with a spacing

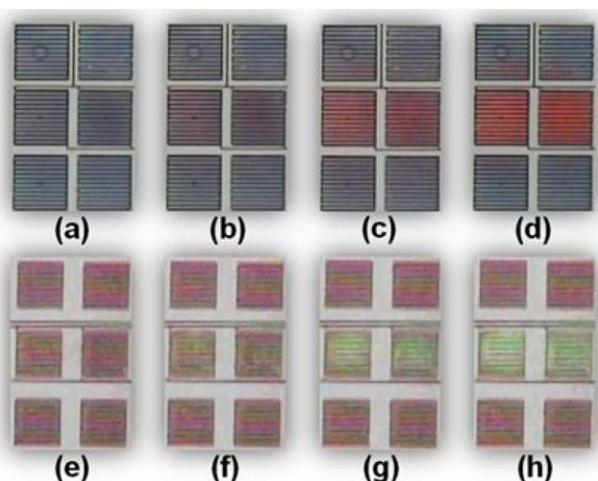


Figure 3. Images captured by a CCD camera of pixel arrays during device activation. The activation potential for the $700 \times 700 \mu\text{m}^2$ array is (a) the off state, (b) 4 V, (c) 5 V, and (d) 6 V. The middle row of the $500 \times 500 \mu\text{m}^2$ array (e-f-g-h) was activated by 10 V pulses with a pulse width of 250 milliseconds. The images were captured sequentially in the time of one pulse width.

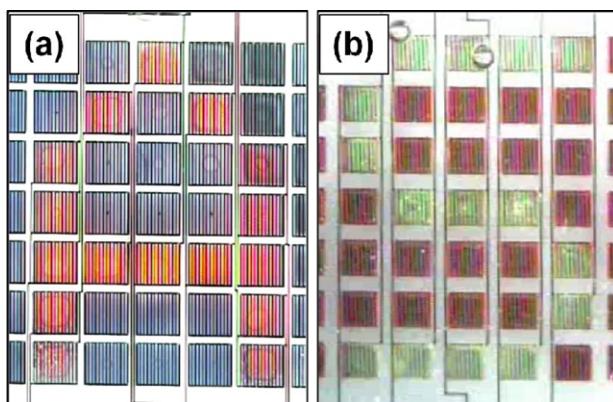


Figure 4. Images captured by a CCD camera of pixel arrays during device activation. The activation potentials for the arrays are (a) 6 V and (b) 10 V, respectively. Actual images are brighter than CCD-captured ones.

of 200 μm . First, the array was continuously driven by DC voltage until a red background was obtained, and the middle row was then switched by 10 V pulses. At the end of a 250 millisecond pulse width, active pixels with a green color were achieved, as depicted in Figure 3(h). The green pixel at 190 $^\circ\text{C}$ without any cross-talk effect is a sign of local heat generation and shows the superior isolation among the micro-pixels.

Figure 4 displays CCD camera images of pixel arrays selectively activated to represent letters A (Figure 4(a)) and S (Figure 4(b)). It should be noted that the actual images seen under a microscope are much clearer and brighter than those captured by the CCD camera.

Conclusions

We have developed a display system based on thermo-chromic conjugated polydiacetylenes. The pixel-images on the display device were patterned using an embedded photomask that provided a self-align method and reduced the complexity of the pixel generation process. The embedded photomask was fabricated from a SU-8 layer that also functioned as a thermal isolator between the adjacent cells. The color cycle from blue to green was achieved by a thermo-chromic change of the color of the micro-pixels. This thermochromic change was triggered by the thermal energy provided by underlying micro-heaters with the aid of controlled voltage pulses. Although the display system described above is not ideal for practical application, the strategy developed should be interesting and could be considered as an important contribution to the application of PDA-based materials.

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