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Development of multi-layer electrochromic polymer display for remotely tunable green-cyan contact lens

A. Khaldi*, H. Menez, Q. Murat, X. Sallenave*, F. Vidal, P-H. Aubert, L. Dupont and J-L. de Bougrenet de la Tocnaye

A. Khaldi, H. Menez, Q. Murat, L. Dupont, J-L. de Bougrenet de la Tocnaye Optics Department, IMT Atlantique, CS 83818, 29238, Brest CEDEX 3, France E-mail: alexandre.khaldi@imt-atlantique.fr; xavier.sallenave@cyu.fr

X. Sallenave, F. Vidal, P-H. Aubert

LPPI, CY Cergy Paris Université, Cergy 95000, France

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ABSTRACT

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The design of the electrochromic component of an instrumented contact lens (ICL) capable of dynamically modifying its color is presented. The device is based on two electrochromic pi-conjugated polymers (CPs) deposited on two electrodes separated by an electrolyte medium. Yellow and cyan electrochromic CPs with two colour states are combined to provide tuneable tint eye iris, from green to cyan colors. The device can switch from green, in which both electrodes are colored, to cyan, in which only the cyan electrode is colored. The additive microsystem process with successive assembling steps allowing the realisation of the bichromatic cell in scleral contact lens is presented as well as the characterization of the colorimetry and switching dynamics.

INTRODUCTION

Instrumented contact lenses (ICLs) are currently gaining significant interest due to their potential use as biosensors¹, for drug delivery², augmented reality³, and color vision management⁴. ICLs were first developed towards the objectives of health management and disease monitoring⁵. Additional features, such as gaze detection for Augmented reality / Virtual reality (AR/VR) displays, have also been suggested⁶ to enable

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information filtering directly on a contact lens, which is beneficial for human-computer interaction⁷.

However, the implementation of ICLs combining complex electronic functions, such as energy collection and storage, optoelectronic functions^{8–10}, biochemical activities if required and electrical transduction, remains a challenging task. Of all these challenges, the most important is miniaturization, which is required to develop a complete device that can be inserted into a single contact lens.

Most current contact lenses have fixed optical properties, including optical power, color, transparency/opacity and refractive index. Although numerous studies have investigated instrumented contact lenses capable of dynamically modifying their color, certain technologies explored^{4,11} do not allow the easy control of the color variation, such as those involving thermochromic⁴ or photochromic materials¹². However, technologies based on electrochromic materials make it possible to change color and opacity almost instantly with a simple electrical command¹³. Therefore, electrochromic based ICLs have been developed to filter light as sunglasses, where only the variable optical density is placed in front of the pupil and can be controlled by the user or adjusted automatically by light sensors embedded in the lens¹⁴. These electrochromic devices have also been used to trigger alarms in response to critical situations, as part of a real-time intelligent health system¹⁵.

Electrochromic materials can be divided into two types, i.e., inorganic electrochromic materials and organic electrochromic materials. Inorganic electrochromic material such as Prussian Blue (PB) has been already proposed for the direct transfer of data through color changes. The ICL is made of two concentric in plane PB-based electrodes, one is for the working electrode (WE), the other for the counter electrode (CE). By applying a voltage, redox reactions occurring at the electrodes trigger reversible changes in color from colorless to blue⁹. Organic materials such as pi-conjugated polymers (CPs), have been also used for ICL. Organic electrochromic material exhibits faster response times and higher staining efficiencies than inorganic ones, even if they have lower UV stabilities¹⁶. Among CPs, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), is a polymer that is commonly used in various electronic and optoelectronic applications. It possesses a range of interesting properties among them its chemical stability under many environmental conditions that make it useful for a variety of applications including electrochromic devices^{17–19}. Thus PEDOT:PSS has

the online version of record will be different from this version once it has been copyedited and typeset is the author's peer reviewed, accepted manuscript. However, been incorporated as an electrochromic material in ICLs, enabling color variation from pale blue to deep blue. The electrochemical cell consists of a PEDOT film as the working electrode and Ag wire as the counter electrode²⁰. Nevertheless, these already reported electrochromic ICLs are monochromatic devices only capable of switching from colorless to blue. However, one could take advantage that CPs offer a wide range of colors to develop a multi-chromic contact lens. Indeed, CPs allow reaching numerous colors by finely engineering it at the molecular level¹³. As electrochromic materials, CPs belong to the subtractive color system and present the advantage to modify their color during their redox process at low voltage¹³, keeping their optical states once the voltage is removed. This low voltage steering is compatible with the on-board electronics on an ICL and the existence of two steady states avoids maintaining a voltage, except for switching the states. Furthermore, CPs are easy to process due to their solubility in many organic solvents, which allows them to conform to a wide range of volumes and surfaces.

Here we report the fabrication of an electrochromic contact lens able to switch between green and cyan colors with a simplified electrochemical cell architecture for an easy integration into instrumented contact lenses. To obtain an electrochromic cell that can be integrated into contact lenses, as reported in^{15,20}, two in-plane electrodes (working and counter) can be designed, but at the cost of a loss of active surface area and complexifying the substrate pre-treatment with an etching step. Therefore, the preferred geometry is two electrodes facing each other, separated by the electrolyte. The WE and the CE is here a combination of two CPs displaying two primary colors. In this proof of concept, we have chosen cyan and yellow CPs to make the device switching from green to cyan colors. The cyan and the yellow CPs selected are the poly[3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-alt-2,7-(9-octyl) carbazole) and the poly[bis[3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4dihydro-2H-thieno[3,4-b][1,4] dioxepine]-alt-benzothiadiazole)) respectively. The yellow CP will be the WE electrode and will face the cyan CP as the CE. The electrochromic CPs are adjusted in quantity such that upon applying voltage the yellow polymer switches from yellow to achromatic state while the cyan polymer stays colored and serves as counter electrode that provides the electric charges necessary for the redox reaction. In this way, the device can be switched from green, in which both electrodes are colored, to cyan, in which only the CE is colored. This simple design

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allows the easy integration of electrochromic polymer into the contact lenses. Thus, we further describe the manufacturing and assembling steps to provide electrochromic iris (or pupil), in compliance with the volume available to encapsulate the various constitutive elements such as the electrochromic materials, the electrolyte, the conductive tracks. Finally, a first proof of concept of a miniaturized switchable electrochromic cell that fit in a scleral contact lens is demonstrated.

RESULTS AND DISCUSSION

Choice of the pi-conjugated polymer as electrochromic materials

The purpose is to change the iris color of the eye from green to cyan on demand thanks to the helps of an electrochromic polymer based ICL. To achieve such color switching, cyan and yellow layers are superimposed, the resulting color is green and changes to cyan when the yellow layer becomes achromatic. Electrochromic cyan and yellow materials are therefore desirable. Polythiophenes are a class of pi-conjugated polymer and are of interest as electrochromic materials due to their ease of chemical and electrochemical synthesis, environmental stability, and processability. A large number of polythiophene derivatives has been synthesized, with interesting properties since subtle changes in the polymer backbone or substituents can significantly alter the optical spectral properties, which is a major advantage for electrochromic applications^{21,22}. For cyan, the spectrum must have a maximum absorbance at 680 nm (band gap close to 1.5 eV) and a minimum at 480 nm. The use of donor-acceptor piconjugated polymers as the poly[3,3-bis(((2-ethylhexyl) oxy)methyl)-3,4-dihydro-2Hthieno[3,4-b][1,4]dioxepine-alt-2,7-(9-octyl) carbazole) allows to reach such a low band gap. The yellow electrochromic polymer chosen from the polythiophene derivatives is the poly[bis[3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4] dioxepine]-alt-benzothiadiazole)). Their chemical synthesis has been described elsewhere 17,23 and these polymers are coloured and achromatic in their neutral and oxidized states respectively. The Figure 1a-d shows the chemical structures of the polymers, their coloured states and their visible absorption properties in their neutral state. The electrochemical behavior of the cyan and yellow polymers were first individually studied by cyclic voltammetry in a 3-electrodes configuration cell using 0.1M Et₄NBF₄/ACN as electrolyte (Figure 1e-f). The electrochromic polymers coated on PET-ITO exhibit reversible oxidation (p-doping) at low potential, around 0.71V and

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0.83V for the forward anodic peaks (Epa) for the cyan and yellow polymers respectively; the backward cathodic peaks (Epc) being 0.54V and 0.68V, respectively. The donor-acceptor-donor structure of the cyan electrochromic polymer allows for n-doping process starting at -1V as shown on the CV of Figure 1e.

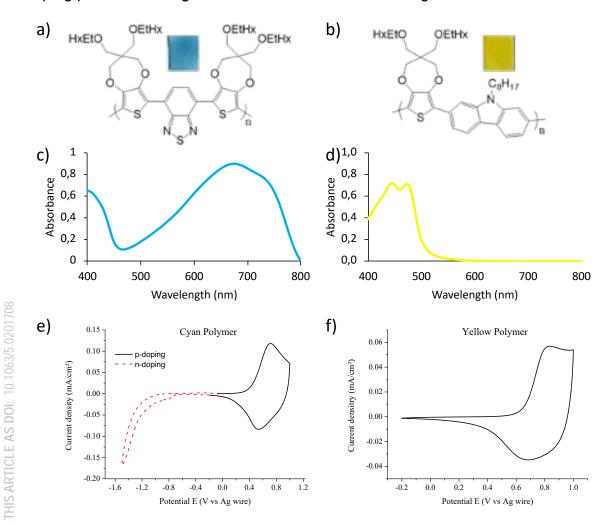


Figure 1: a) and b) Chemical structures of cyan and yellow CP and their corresponding colors in the neutral state, c) and d) UV-Vis absorption spectra, e) and f) cyclic voltammetry characteristics of cyan and yellow conjugated polymers.

Principle of the electrochromic cell architecture and electrochemical experimental simulation

An electrochromic cell is an electrochemical cell, in which two transparent electrodes coated with CP are facing each other, in the presence of an electrolyte. In this study, the electrolyte is 1-Ethyl-3-methylimidazolium bis(trifluoromethane-sulfonyl)imide (EMITFSI), encapsulated between two transparent PET-ITO substrates on which the two yellow and cyan polymers are coated. The yellow layer is set as WE whilst the

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cyan one is the CE. The Figure 2 shows the working principle of the electrochromic cell. When cyan and yellow polymers are in the colored state, the resulting color is green. To achieve color tuning from green to cyan, the yellow layer should become achromatic while the cyan polymer should remain colored. Therefore, an adequate balance of yellow and cyan polymers in terms of thicknesses and electrical charges passed should be achieved to obtain optimal colorimetric change and to balance the yellow oxidation and reduction while keeping its cyan state with minimal optical change during the redox reaction.

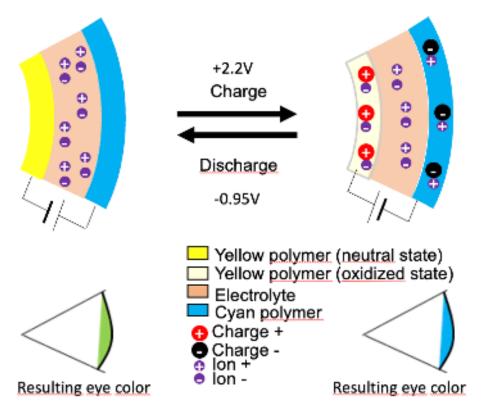


Figure 2: Schematic of the working principle of complementary color electrochromic display. There is an excess of cyan polymer causing stable coloration of the layer; in a discharge state, the yellow polymer remains yellow causing the display to be green; in a charged state, the yellow polymer becomes transparent causing the display to appear cyan.

For a better understanding of the behavior of the electrochromic ICL, we mimic first the device in a 3-electrode cell configuration using yellow and cyan as WE and CE, respectively, and a silver wire as reference electrode. This setup allowed the recording of both the current density passing through the yellow (WE) and cyan (CE) electrodes This is the author's peer reviewed, accepted manuscript. However, the online version of record will be different from this version once it has been copyedited and typeset

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and potentials of the cyan CE (E_{ce}) during the switching (Figure 3). Before starting the electrochemical characterization, the open cell voltage (OCV = EWE - ECE) is around -0.95V due to the initial pre-conditioning of the two polymers: yellow and cyan were maintained at -0.2V and 0.75V, respectively. At these potentials, the WE CP is dedoped and exhibits its bright yellow color while the cyan polymer is partly oxidized, but still colored. Upon switching to $E_{we} = +1.0V$ to fully oxidize and bleach the yellow polymer (Figure 3 black curve), the Ece decreases, hence the cyan polymer process first to p-dedoping within the potential range [$+0.75V \rightarrow 0V$], then evolves promptly to a potential of -1.2V (Figure 3 red curve), corresponding to the beginning of its *n*-doping process. So, to perform the ICL cell switch, a voltage of 2.2V should be necessary. It must be mentioned that during the *n*-doping at -1.2V, the cyan color is also maintained. In other words, to achieve the cyan color of the ICL device, the cyan polymer must undergo p-dedoping then n-doping process. As said before, its amount should be adjusted to keep the polymer color unchanged during the optical switching of the yellow polymer. For a good balance, the cyan layer used as a counter-electrode shows a charge capacity of 2.5 mC/cm², higher than the yellow one (0.8 mC/cm²). It is worth mentioning that thanks to the donor-acceptor character of the cyan polymer, the ndoping process can proceed without causing harm to the electrochemical cell's constituents, i.e. without irreversible side-reactions neither from the electrochromic polymers nor the electrolyte.

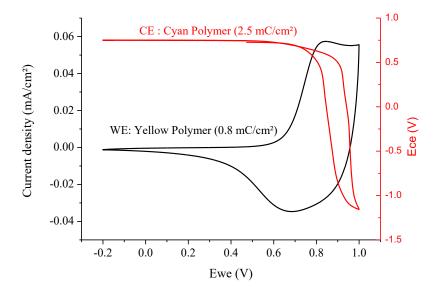


Figure 3: (black curve) Cyclic voltammetry of the Yellow polymer (0.8 mC/cm²) in a 3-electrode setup utilizing the Cyan polymer as CE (2.5 mC/cm²). (red curve) evolution

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of the potential of the counter electrode (Ece) as function of the potential of the working electrode (Ewe).

Electrochromic ICL manufacturing

The first step for manufacturing the ICL is to develop a robust microsystem additive process to produce the miniaturized electrochemical cell. The developed microsystem additive process is schematized on Figure 4 and allowing the preparation of 4 ICL displays at the same time. A PET-ITO substrate (thickness 175 μ m) is used and supplied with a protective layer on each side. The protective layer is removed from the ITO surface when the other remains onto the PET surface. A laser ablation of PET-ITO layer is realized without damaging the protective layer on the back to create a hinge to ease the assembly process. Then, successive depositions of both CPs with the aerograph are realized and the quantities have been optimized. Absorbances in the visible range of 0.9 and 0.7 are sought after for the cyan and yellow CP respectively corresponding to approximatively 2.5 mC/cm² and 0.8 mC/cm² for cyan and yellow polymers, respectively as mentioned previously. The Su-8 is deposited on the yellow CP layer under a shape of two circles at a standard iris size (12 and 3.5 mm diameter) to create the electrochemical cavity. The resulting SU-8 wall thickness is approximately 100 μ m. UV-S 91 adhesive is then applied around both SU-8 walls without contaminating the electrochemical cavity. To enable automatic filling of the electrolytic cavity, the electrolyte solution is then thickened by dissolving 30 wt% of polyethylene glycol (PEG, 1500 g.mol⁻¹) in EMITFSI to adjust the viscosity. The method that allows the cell to be perfectly filled without trapping bubbles is to print this electrolyte solution in the form of a circle between the two SU-8 walls. The following step is to fold the substrate thanks to the hinge initially created. The UV-S91 adhesive is then exposed to UV light to seal the device. The final steps of the process are the laser ablation of the full device and, locally on the contact pads, knotting of an electrical wire and ensure connection with an Aq lacquer. The device is then connected to a potentiostat for switching.

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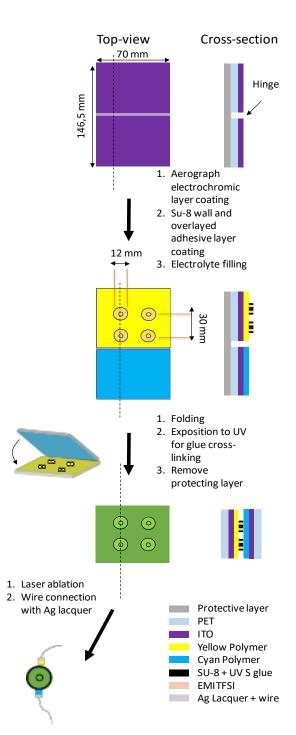


Figure 4: description of the additive microsystem process.

Colorimetric ICL charaterization

Once assembled with the right proportion of electrochromic polymers and electrochemical preconditioning (vide supra), both CPs present their colored neutral states cyan and yellow, resulting in a green appearance. When the device is switched at +2.2V, the yellow polymer oxidizes resulting in the bleaching of the layer; at the same time a reduction occurs on the cyan polymer but without color change. The This is the author's peer reviewed, accepted manuscript. However, the online version of record will be different from this version once it has been copyedited and typeset.

resulting color of the switched state is then a cyan appearance (Figure 5a and video S1). With this device, the colorimetric changes are localized in the area corresponding to the iris of the eye. This part can be removed, for instance, by laser ablation to leave the pupil free or by protecting the pupil area during aerograph deposition of electrochromic polymers. The resulting color on CIE 1931 diagram is shown Figure 5b using D65 reference as a light source. Finally, the miniaturized cell is then integrated alone (without its electronics) inside a scleral contact lens, indicating its ability to be integrated into such a reduced volume (Figure 6). We describe here the principle of encapsulation of such device into a scleral contact lens. The electrochromic cell and further its driving electronics could be sandwiched between 2 pre-manufactured pucks which would be sealed together before the upper and lower surfaces would be lathed to manufacture the lens curvatures and to obtain the final wearable contact lens.

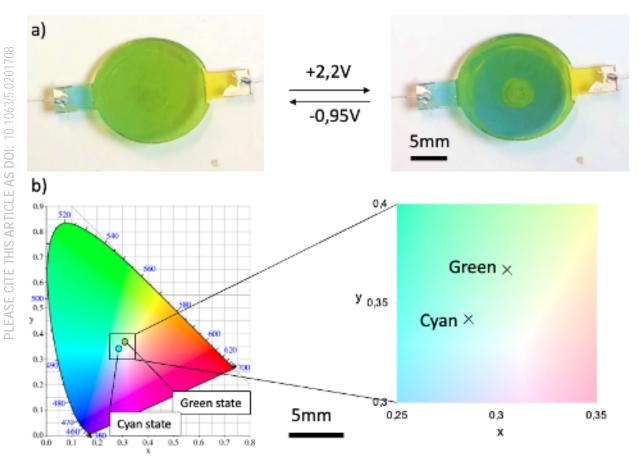


Figure 5: Electrochromic display operation; a) color change of the electrochromic display, b) report of colorimetric characteristics of the display in Green and Cyan states in CIE 1931 diagram (Green: x=0,3048, y=0,3668; Cyan: x=0,2855, y=0,3323).

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Figure 6: Integration of the electrochromic display in a scleral contact lens

CONCLUSION

The first objective of this study was to design the electrochromic component of an instrumented contact lens (ICL) capable of dynamically modifying its color. A bichromic ICL was easily developed by using two electrochromic polymers, yellow and cyan, in a face-to-face electrode configuration. A proper balance of each electrochromic polymer controls the device's ability to switch between green and cyan color states. During the switching process, the yellow layer becomes achromatic while the cyan polymer remains colored. The donor-acceptor character of the cyan polymer enables the n-doping process necessary for this color switch. The applied potential/voltage allowing the switching is compatible with the embedding of a drive. The proof-ofconcept for this bichromatic lens was performed using the ionic liquid EMITFSI as the electrolyte. It is known that EMITFSI ionic liquid can be harmful, which is why the next generation of electrochromic ICLs will use deep eutectic solvents (DES). Indeed, DES are a good alternative to ionic liquids if the combination of partners is well chosen. They can be non-volatile like ionic liquids and present no health risk to users. In the second part, we had to demonstrate that the size of the bichromatic cell was compatible with that of a scleral contact lens. The additive microsystem process described enables four bichromatic cells to be prepared in a single operation and each of them can then be inserted into a scleral contact lens as designed.

The extension to three colorimetric states is the focus of future work to offer additional color options. For example, with a new electrochromic cell design, magenta polymer can be added to the cyan and yellow polymers, or trichromatic polymers can be used²⁴.

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In terms of technology, the next challenge is to optimize the encapsulated volume. This can be achieved by reducing the thickness of cell substrates and preforming or molding the cell to fit the curved shape of the contact lens meniscus. In addition, the cells can be stacked in a double-layer structure together with their control electronics.

EXPERIMENTAL SECTION

Materials

UV-S 91 was ordered from Edmund optics, SU-8 2025 was ordered from Microresist technology (Germany), PET-ITO substrates were shipped by Vision tek systems Ltd (UK). Poly(ethylene glycol) (PEG 1500), acetonitrile (ACN) and tetraethylammonium tetrafluoroborate (Et₄NBF₄) were ordered from Merck and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) (99.9% purity) from Solvionic (France). Ag lacquer ferro L200N was supplied from CDS electronique (France). Cyan and yellow conjugated polymers have been synthesized by a method described in¹7,23. CP solutions were prepared by dissolving cyan and yellow polymers in toluene at 3 and 1.5 mg.mL⁻¹ respectively. After stirring the materials during 24 hours at room temperature, both solutions were filtered with 0.45 μm pores filters before spray deposition with aerograph.

Electrochemical characterization

Gamry 1010E potentiostat was used to characterize electrochemically the electrochromic CPs single layers and trigger the commuting of the final device. To characterize the single layers of ECPs by cyclic voltammetry at 20 mV/s, 3-electrodes electrochemical cell with an Ag wire as a reference electrode and 0.1M Et₄NBF₄/ACN electrolyte was used. The silver reference electrode was calibrated with 5mM ferrocene redox probe in same electrolyte providing apparent redox potential at 0.435V.

Optical characterization

A HR-4000 spectrometer from Ocean Optics and a tungsten halogen light source HL-2000 were used to measure the transmission spectra of the samples at normal incidence. Then, using the color matching functions proposed by the International Commission on Illumination (CIE), we calculated the tristimulus values (e.g. XYZ by colours) and the colorimetric coordinates CIE-1931 for standard D65 white light source.

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Electrochromic ICL manufacturing

A thermoflan series v2000 laser ablation, dispenser EFD ultra TT series deposition system, aerograph lwata absolute precision CM-B were used for additive microsystem process.

The colorimetry of deposited layers has been optimized empirically, and we obtained satisfying results with maximum absorbance in the visible range of 0.9 and 0.7 (35 and 8 aerograph manual scanning deposits) respectively for the cyan and yellow polymers. 100 μ m SU-8 wall is exposed to UV (395 nm) during five minutes at 6.4 mW.cm⁻² power. The UV-S 91 glue is exposed to UV (395 nm) at 6.4 mW.cm⁻² power during 5 minutes. Laser ablation parameters used to cut the full device and single substrates are 27 W and 99 cm.s⁻¹. In these two UV exposition steps, the conjugated polymers are protected with an UV-absorbant paper. However, 16.5 W power and 76.2 cm.s⁻¹ scanning rate laser ablation parameters are used to cut a substrate without damaging the protective layer in order to create a hinge used to ease the assembly process.

SUPPLEMENTARY MATERIAL

Video S1 shows switching dynamics of the electrochromic display.

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Emmanuel Daniel for designing and providing the driving electronics, Vincent Nourrit for sharing the original idea of tuneable tint contact lens, Daniel Stoenescu for the colorimetric testing (all with IMT Atlantique), Laure Adam for designing and manufacturing the host contact lens (LCS laboratories), and Institut Mines Télécom for funding the study thanks to a Carnot Télécom Société Numérique grant.

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