

An Optically Programmable Surface Realized with Azobenzene-Functionalized Lotus Leaf and OLEDs

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Abstract—Spatially programmable surface properties are important building blocks for future microfluidic and biosensor devices. We demonstrate switching of a photochromic surface with a blue organic light-emitting diode (OLED) suitable as an integrated on-chip light source. The surface of a positive polydimethylsiloxane (PDMS) replica of a fresh lotus leaf is covalently functionalized with a photoswitchable azobenzene self-assembled monolayer (SAM) employing “click chemistry.” 80 % of the azobenzene molecules are switched from *cis* to *trans* state within 4 min of OLED irradiation. A spatially resolved study of the azobenzene switching properties on the naturally inhomogeneous lotus surface is conducted evaluating the transmission of a 355 nm laser beam. In the area of the leaf veins the highest change in the relative transmission of 100 % is obtained upon switching from *trans* form to *cis* form under UV illumination. In comparison, an azobenzene-functionalized flat glass surface exhibits only a 0.5 % change in the relative transmission.

Index Terms—Biomimetics, biosensors, organic light emitting diodes, photochromism, surface engineering, surface structures, thin film devices.

I. INTRODUCTION

IN recent years, more and more functionalities have been shown with photochromic molecules, controlling, e. g., adsorption and desorption of proteins or ligands [1] or adhesion of cells [2], [3]. This promises superior spatiotemporal control in devices [4] and all these functionalities can be realized on surfaces [5], [6]. Stilbens, azobenzenes, diarylethenes and spiropyranes are photoresponsive chromo-phores [7]. Azobenzene has been popular for switching applications with biomolecules [6]. This molecule has two phenyl rings connected with a nitrogen double bond and possesses two isomeric states. The thermally stable one is the *trans* state and the second one is the *cis* state. A switching between these states is achieved by using ultraviolet (UV) light from the *trans* to the *cis* state or visible (mainly blue) light from *cis* back to *trans*. As azobenzene is a photochromic molecule, its different states are distinguished by their absorption characteristics in photospectrometric measurements. This changing absorption is utilized for visualizing a changing surface property and it is not

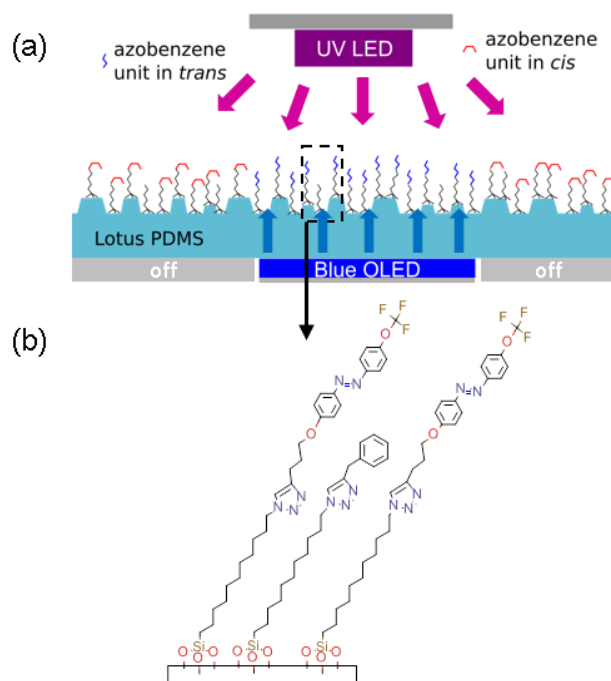


Fig. 1. (a) Schematic of device for programming surface properties: artificial lotus leaf functionalized with a SAM of azobenzene molecules excited by a blue OLED. (b) Schematic of azobenzene attached to surface with phenyl derivative in between to prevent steric hindrance.

the modulation of light that is mainly aimed as applications. Usually, bulky light-emitting devices such as lasers or mercury vapor lamps are used to excite photochromic molecules. Here, we investigate the use of organic light-emitting diodes (OLEDs) for switching layers of azobenzene molecules. OLEDs are thin area light sources [8] that are commonly used in displays. Their applications in sensors [9], [10] and even for optogenetic control [11] have been demonstrated. An artificial lotus leaf substrate is employed for increasing the transmission change upon switching. The concept for an optically programmable surface is depicted in Fig. 1. The use of a single UV LED is proposed to switch the entire surface to the *cis* state. This “erases” the spatial information. The UV LED could be integrated in the lid of a microfluidic device. An array of blue OLEDs allows for spatially resolved “programming” of the

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surface properties by switching parts of the surface back to the *trans* state.

For integrated sensors, both the functionality of the molecule itself as well as the attachment of the molecules to the surface are highly relevant. To produce stable layers covalent coupling is preferred, forming a self-assembled monolayer (SAM). For sensing purposes, the number of molecules per surface area has an important influence. Due to their single-layer configuration, SAMs on flat surfaces offer a limited molecular density. Higher densities are achievable by enlarging the surface with micro- or nanostructures. Combinations of micro- and nanostructures occur in nature with the lotus leaf being a prominent example [12]. Sun *et al.* [13] introduced a nanocasting process for replicating a lotus leaf into polydimethylsiloxane (PDMS). PDMS can be used for the fabrication of fully flexible devices and is biocompatible [14].

Here, we utilize the functionalization of an artificial PDMS lotus leaf based on a variation of the process by Sun *et al.* with azobenzene molecules. This functionalization is achieved by a silane attachment with its modification to an azide-terminated monolayer and mounting azobenzene molecules by a 1,3-dipolar cycloaddition known as “click reaction [15].” The produced surfaces are highly transparent and are switched with a UV LED and a blue OLED with 4,4'-Bis(9-ethyl-3-carbazovinylylene)-1,1'-biphenyl (BCzVBi) as emitters [16], [17]. Additionally, a spatially resolved study of the switching properties of the naturally inhomogeneous azobenzene-functionalized artificial lotus leaf is presented. For this purpose, we scan the transmission of the sample with a laser at a wavelength of 355 nm, where the absorption difference of azobenzene *cis* and the *trans* isomers is high.

II. EXPERIMENTAL

A. Materials and equipment

Toluene, dimethyl sulfoxide (DMSO), sodium azide, copper sulfate pentahydrate, molybdenum(VI) oxide (MoO₃), N,N'-Di-[(1-naphthyl)-N,N'-diphenyl]-1,1'-biphenyl)-4,4'-diamine (NPB), bathophenanthroline (BPhen), lithium fluoride (LiF) and 3-phenyl-1-propyne were purchased from Sigma Aldrich. Isopropanol, ethanol and double distilled water were obtained from Roth. PDMS / Sylgard 184 was bought from Dow Corning and bromoundecyltrichlorosilane from ABCR. The azobenzene molecule was synthesized by ChiroBlock GmbH, Wolfen (Germany) according to known synthesis instructions [18], [19]. Indium tin oxide (ITO) covered glass slides were purchased from PGO GmbH, Iserlohn (Germany). 4,4'-Bis(2,2-diphenylethenyl)-1,1'-biphenyl (DPVBi), BCzVBi came from BOC Sciences, Shirley, NY (USA) and the aluminum was from Kurt J. Lesker.

The UV laser used for the experiments was a Cobolt Zouk CW 355 nm and the translation stage was a ProScan II system by Prior. Absorption measurements were performed using a PerkinElmer Lambda 650 and the contact angle measurements with an OCA50AF by Dataphysics. The employed LEDs were a Nichia NCSU033B with a peak wavelength of 365 nm and a Luxeon LXML PR01 0500 emitting at 448 nm.

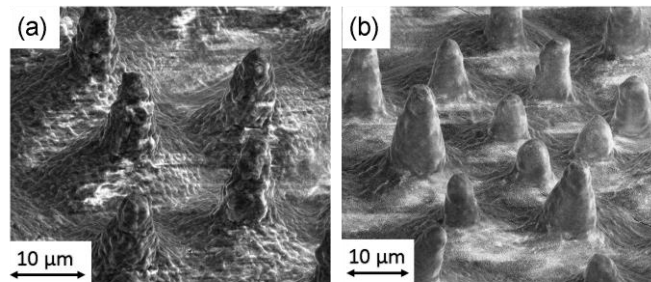


Fig. 2. SEM image of artificial PDMS lotus leaf (a) before and (b) after treatment with oxygen plasma.

B. Molding of the PDMS lotus leaf

The two-component system Sylgard 184 is mixed according to the supplier instructions and poured onto a flattened fresh lotus leaf. Full polymerization is reached after two days at room temperature. This step is not accelerated with heat, as heat would destroy the leaf and produce gas bubbles in the PDMS. After polymerization, the lotus leaf is removed from the negative PDMS copy and a 5 nm gold layer is thermally evaporated on top of the structure as an anti-sticking layer. Next, Sylgard 184 is poured onto the negative PDMS copy to regain a positive copy of the original lotus leaf. The sample is stored under a low vacuum for 45 min to remove bubbles produced by the mixing. The PDMS is heated to 90 °C to polymerize within two hours. Afterwards the back of the positive copy is treated with an oxygen plasma of 100 W radio-frequency (RF) power for 1 min and bonded onto a glass substrate. This is needed to prevent swelling during a later toluene bath and for handling. Finally, the two PDMS parts are separated.

C. Azobenzene functionalization

Next, the artificial lotus leaf is functionalized via silanization and subsequent “click reaction.” A gentle oxygen-plasma treatment for 30 s at 50 W RF is used to obtain free OH-groups on the PDMS surface. These are needed for attachment of trichlorosilane as the anchor group. The samples are placed in a toluene solution containing 0.005 vol% 11-bromoundecyltrichlorosilane for 30 min to realize a monolayer of the silane on the PDMS. Afterwards, they are washed with dried toluene three times. Both steps are conducted in a pure nitrogen environment. Next, the terminal bromide group of the silane is exchanged with an azide group. For this purpose, the samples are rinsed for 10 min in toluene and DMSO. The azide exchange is obtained within two days in a saturated solution of sodium azide in DMSO. Usually, this is done at higher temperatures [3], [15]. In order to protect the PDMS layer from swelling we performed this reaction at room temperature [20]. Subsequently, the samples are rinsed for 5 min in DMSO, double distilled water and isopropanol. The 1,3-dipolar cycloaddition is performed by placing the samples in an ethanol solution with a total concentration of 2.0 mM (4-pent-4-ynyloxy-phenyl)-(4-trifluoromethoxy-phenyl)-diazene (OCF₃-

Azo) and 3-phenyl-1-propyne (ratio of 1:1). To 22 mL of this solution we add 800 μL of an aqueous solution, where 30 mg of sodium ascorbate and 30 mg of copper sulfate pentahydrate have been suspended in 3 mL of double distilled water. The alkyne 3-phenyl-1-propyne is added to prevent steric hinderance [21], [22]. The last reaction is executed at room temperature with stirring at 200 rpm for two days. Finally, the samples are rinsed in ethanol, isopropanol and distilled water. For comparison, a flat quartz glass substrate is functionalized by the same procedure.

D. Surface characterization

For the characterization of the samples, we perform contact angle measurements and prepare scanning electron microscopy (SEM) images. Additionally, we map the transmittance of the functionalized PDMS surface to investigate the absolute transmission as well as the switching properties of the surface. Normal-incidence transmission measurements are performed with a continuous-wave UV laser with a wavelength of 355 nm. The laser is operated with an external shutter to prevent unwanted switching. The sample is scanned across the laser beam with a high-precision microscope translation stage. The transmitted beam power is measured with a photodiode behind the sample. A second photodiode in a reference arm is used to calculate the transmittance.

E. OLED fabrication

ITO-coated glass substrates are structured with a standard lithography process and etching in hydrochloric acid (30 %). The samples are thoroughly cleaned in an ultra-sonic bath with acetone and isopropanol each for 10 min. After 10 min dehydration on a hotplate at 160 $^{\circ}\text{C}$, the ITO is activated with an O_2 plasma with 300 W RF power for 4 min. Next, a stack with MoO_3 (10 nm) / NPB (20 nm) / DPVBi:BCzVBi 5 % (20 nm) / BPhen (30 nm) / LiF (0.6 nm) / Al (200 nm) is thermally evaporated on top of the ITO. The organics are then encapsulated with an epoxy adhesive and an additional glass slide.

III. RESULTS

An SEM image of the non-functionalized PDMS artificial lotus leaf is shown in Fig. 2a. The typical micro- and nanostructures of the lotus leaf are clearly visible. The micro pillars have an average height of 8.5 μm . Both for the artificial leaf and the natural leaf contact angles of water droplets of $>150^{\circ}$ are measured, which are close to values given in other publications [12], [23]. In the SEM image in Fig. 2b it is seen that the plasma treatment damages the nanostructure. The contact angle for water droplets on the surface after treatment with an oxygen plasma is decreased to 110° . After the functionalization with the azobenzene the contact angle of water droplets is $\sim 110^{\circ}$ on the samples. No difference in the wettability is observed between the *cis* and the *trans* isomers.

The fabricated blue OLED emits light with a peak wavelength of 470 nm, which lies well in the $n-\pi^*$ transition band (410 nm–500 nm) of the azobenzene layer (Fig. 3). The

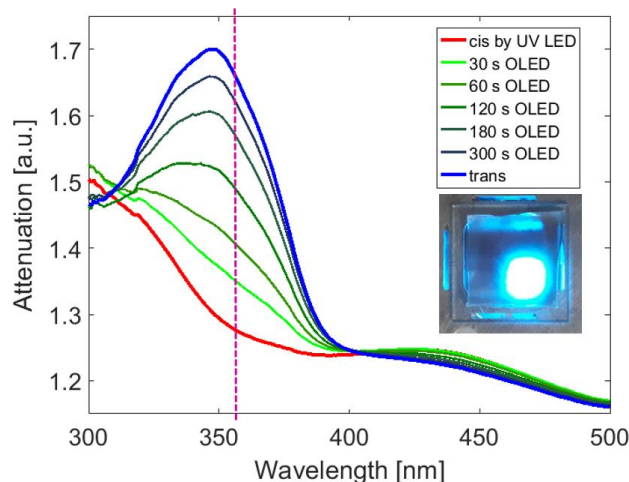


Fig. 3. Attenuation spectrum of sample with successive switching by blue OLED, dashed line shows position of laser emission for surface scanning; Inset: Photograph of lotus PDMS with OLED excitation from the back.

device emits a radiant flux of more than 10 mW/cm^2 , but is driven at a lower current to prevent degradation. For LEDs on top of the device and the OLED at the bottom of the substrate, we measure the emission intensities at the first surface border of the lotus PDMS (see Fig. 1(a)). Fig. 3 shows the absorption measurements of the azobenzene layer after different irradiation steps. First, the high-power UV LED (96 mW/cm^2) is used to switch from the *trans* state to the *cis* state. Then the blue OLED (4 mW/cm^2) is turned on for different time spans. After four minutes, 80 % of the azobenzene molecules are switched back to the *trans* state. With an increase of the radiant flux a faster switching would occur but simply doubling the energy input will not result in a doubling of the switching speed due to different lifetimes, saturation and quenching [21], [24].

Fig. 4a shows a photograph of the azobenzene-functionalized artificial lotus leaf. The macroscopic inhomogeneity of the surface with the leaf veins is visible. The transmission is mapped at a wavelength of 355 nm, because at this wavelength the absorption difference of the azobenzene *cis* and *trans* isomers is high (see Fig 3). The power of the UV laser is low enough (10 μW on the incidence side) such that it does not induce a significant switching of the azobenzene layer into the *cis* form. During a measurement step, the shutter is opened to allow the beam the exposure of the surface for half a second. Then the shutter is closed and the sample moved by a stage to the next position. As seen from Fig. 4d the laser needs over 200 cycles at the same point on the PDMS sample to cause a complete switching to the *cis* state. On a flat glass substrate, the *cis* state is reached two times faster, but Fig. 4e also illustrates that the relative transmission change is only 0.5 % compared to 100 % for the artificial lotus-leaf substrate.

In our measurements, the laser scans each point only once to prevent further switching of the molecules. This limits the resolution to the spot diameter of the laser beam, which is 800 μm for our setup. Fig. 4b shows a transmission map of the sample with all azobenzene molecules in the *trans* state. The leaf veins are clearly visible. They exhibit a higher transmission than other areas of the leaf by a factor of 1.70 ± 0.29 . The artificial lotus leaf is then covered with a plate containing a

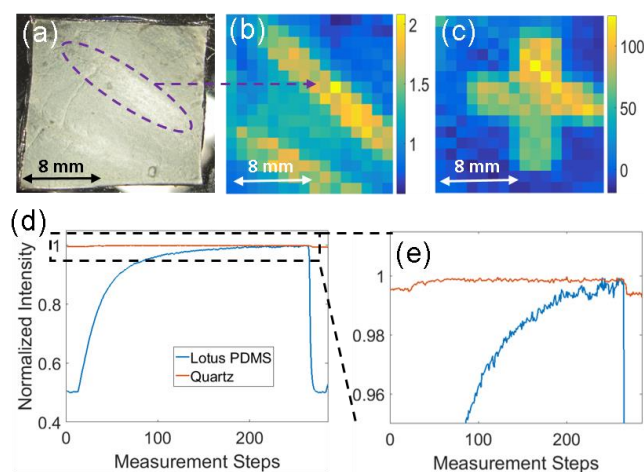


Fig. 4. (a) Photograph of the lotus PDMS; (b) Transmission map of the sample before UV exposure normalized to the first measured point (first “pixel” in the upper left corner). Leaf veins are clearly visible—all molecules are present in the *trans* state; (c) Percentual transmission difference of a scan after partial UV-light exposure (cross mask) to the same surface as in (b), the resolution of the maps is limited by the diameter of the laser beam; (d) Measurement of UV laser intensity with comparison of induced switching of azobenzene on lotus PDMS and flat quartz from *trans* to *cis* and back to *trans* with magnification in (e).

cutout in the form of a cross and exposed to a UV LED for 30 s. Afterwards, the sample is scanned again. Fig. 4c shows the difference map of the scans before and after the UV exposure. Only the cross-shaped area not covered by the mask is switched. As can be seen, the switching is higher in the leaf vein area.

IV. CONCLUSION

We transferred a lotus structure into PDMS and covalently bound a single layer of azobenzene molecules on top of the surface. The lotus structure highly increased the normalized relative transmission difference between the *trans* and *cis* state compared to a flat quartz substrate. We created surface maps showing the largest switching effects on the leaf veins. To utilize this for a larger surface, either a new stamp could be assembled from leaf vein sections or the micro-/nanostucture of the veins could be reconstructed artificially. An array of OLEDs is an ideal candidate as an on-chip light source as OLEDs are thin and may be processed on plastic substrates. We demonstrated the switching of a photochromic layer with an OLED. A further improvement in brightness promises a faster switching. The large effect of switching on transmission is promising for programmable sensing surfaces with the switching of binding sites, e. g., for protein binding [5], [25].

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