Tuning the Fluid Wetting Dynamics on Gold Microstructures and Conductivity of Polyaniline Using Photoactive Compounds

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TUNING THE FLUID WETTING DYNAMICS ON GOLD MICROSTRUCTURES AND CONDUCTIVITY OF POLYANILINE USING PHOTOACTIVE COMPOUNDS

by

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Spring Term
2022

Major Professor: Karin Y. Chumbimuni-Torres
To my loving family.

For providing endless support throughout this journey.
ABSTRACT

Organic photochromic compounds (OPCs) are considered as a class of light sensitive compounds that undergo reversible structural transformation of their physicochemical properties (i.e., polarity and charge distribution) upon light irradiation as an external stimulus. These compounds have been extensively studied for decades, and are used in various applications such as biomedicine, chemical sensors and harvesting solar energy. In this thesis, applications of OPCs were investigated under two different projects: 1) controlling wettability of flat and microstructured gold surfaces and 2) controlling the electrical conductivity of polyaniline. The first project demonstrates how photoactive compounds can be used to tune the surface chemistry, surface free energy, and the wetting velocity of fluids on Spiropyran (SP) functionalized surfaces in different microstructured surfaces. In this regard, the wettability was measured using static and dynamic (advancing and receding) contact angles in microstructured surfaces conjugated SP. This study examined the possibility of reversible switching between the static Cassie-Baxter (or Wenzel) state and the dynamic hemiwicking state. Furthermore, by incorporating changes in contact angle into the Owens-Wendt and Van Oss surface energy models, the energy of smooth Au surfaces was predicted upon photoisomerization of SP.

The second project investigated the possibility of photoswitching the conductivity of flexible films based of polyaniline (PANI). The film is composed of a visible light sensitive mixture drop casted on the Polyethylene terephthalate (PET) substrate precoated with a conductive polyaniline emeraldine salt (PANI-ES) layer. The electrical conductivity of the film is modulated by metastable state photoacid (mPAH), which is visible light induced proton transfer compound.
ACKNOWLEDGMENTS

I would like to express my sincerest gratitude to my mentor, Dr. Karin Y. Chumbimuni-Torres. I appreciate that she gave me opportunity and entrusted me to work on her lab. Without her full support and guidance through numerous hardships, the success of this research would not have been possible.

I would like to give my sincerest thanks to all the committee members (Dr. Andres Campiglia, Dr Gang Chen, Dr Andrew Frazer and Dr Woo Hyoung Lee) for providing support throughout my graduate studies and taking the time from the busy schedule to serve as a committee member. I am so thankful for their constructive advises toward my PhD research. A special thanks to Dr. Shawn Putnam and his graduate student Thomas Germain (now Dr Germain) for their significant contribution and providing insights on the microstructure wetting toward the collaborative project. This collaborative project could not be done without your help. I am very grateful to be a part of this great collaboration.
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CHAPTER 1 GENERAL INTRODUCTION

1.1 Reversible Organic Photochromic Compounds

Photoactive compounds such as Reversible Organic Photochromic Compounds (OPCs) can undergo reversible structural transformations such as changing their shape, polarity, and charge distribution when light is irradiated [1]. An external stimulus such as light can be used as a non-invasive and inexpensive source of energy to modulate in a reversible manner a target's properties. A structural transformation of OPCs can be accomplished either by trans-trans double-bond photoisomerization or light-activated cyclization and ring-opening reactions. Azobenzene, diarylethene, and Spiropyran (SP) are three of the most well-known OPCs (Fig. 1). Azobenzene is an example of a trans-cis double-bond photoisomerization, in which the low-energy trans-form and colorless azobenzene is converted to the high-energy cis-form and colored azobenzene upon exposure to UV light. Furthermore, upon exposure to visible light, it returns to its low-energy trans-form and colorless azobenzene [1]. An example of light-activated cyclization is the electrocyclization reaction that occurs upon irradiation with UV light, which converts dithienylethen into a highly energetic, colorless closed form. In general, electrocyclization is a reaction consisting of ring opening and ring closing. As a result of the electrocyclization process, dithienylethen absorbs light in the UV and visible light region depending on the R group (for instance, benzene as the R group would give an absorption peak between 550-600nm in the visible light region). In addition, during the electrocyclization reaction, the conformation of the attached group will change according to the conrotatory ring closure and opening.
In addition, upon exposure to visible light, it reverts to a low-energy open and colorless state [1]. Spiropyran is an example of the last type of structural transformation upon irradiation with light (photoisomerization). The Spiro ring is opened by ring-opening reaction upon exposure to UV light, during which the C-O bond of SP is broken. Under this reaction, the closed-form and hydrophobic SP is converted into the open form and hydrophilic SP (merocyanine) [1].

![Diagram of Spiropyran and Merocyanine]

**Figure 1** Examples of light responsive organic photochromic compounds (a) Azobenzene, (b) dithienylethene, (c) Spiropyran.
A variety of applications for OPCs have been developed including chemical sensors, energy conversion, tuning wettability, and electrical conductivity toward photoswitchable surfaces.

The aim of this thesis is to apply two important classes of OPCs to tune the wettability of gold microstructures and modulate the electrical conductivity of polyanilines. SP was used to tune the wettability of the gold microstructures, and meta stable state photoacid was used to modulate the electrical conductivity of polyaniline. In the following, we will discuss their application in the two research projects.

1.2 Tuning wettability of the gold microstructures using SP:

Microstructures are micro dimensional structures or pillars that are made by adding small elements to the surface to increase surface area and have wide range of applications. Fig. 2 demonstrates the main applications of microstructures. They can be used to dissipate heat in electronic devices (Fig. 2 (a)), as well as for wettability applications (Fig. 2 (b-c)). In terms of heat dissipation, the fabrication of microstructures under the cover of electronic devices can increase the possibility of heat dissipation by distributing the heat over a larger area. Further, microstructures may also be utilized to enhance surface wettability, ranging from superhydrophobic (Fig. 2 (b)) to superhydrophilic (Fig. 2 (c))).
Figure 2 Application of microstructures in (a) heat dissipation in electronic devices, (b) superhydrophobic surfaces and (c) superhydrophilic surfaces

Self-cleaning coatings used in the textile, medicine, and construction industries are examples of superhydrophobic surfaces. Furthermore, superhydrophilic surfaces are of interest to this study (hemiwicking wetting behavior in the microstructures) due to their potential use heat pipe industry (Fig. 2(c)). Fig. 2(c) illustrate the relationship between heat flux (flow of energy per unit of area per unit of time) and wall (surface) temperature of the heat pipe (for both hydrophilic and hydrophobic surfaces). As it seen in this figure 2(c), the critical heat flux (CHF) occurs in the lower heat flux on hydrophilic surfaces (CHF is the temperature range in which the phase transfer occurs during the phase transformation). It represents the higher heat dissipation in the hydrophilic surfaces (microstructure with hemiwicking wetting behavior).
Wetting state of microstructures depends on their specifications such as distance between pillars(s) height(h) and diameter(d). Fig. 3 depicts a close view of microstructures and their specifications. A microstructure's transition wetting is determined by the ratio of the spacing to diameter (s/d) and the height to diameter (h/d). By increasing the spacing between pillars of fixed diameter and height, we can observe wetting transitions between three key fluid wetting behaviors with microstructured surfaces (from Cassie-Baxter to Wenzel states and from Wenzel states to dynamic hemiwick states).

![Image of microstructures with labels](image_url)

*Figure 3 Parameters of microstructures consist of vertical distance between pillars (Sx and Sy, respectively), height(h), diameter(d) and angle between the pillars(α)*

Generally, there are two methods for controlling the wettability of a solid surface. The first one is changing the liquid surface energy, and the second one is changing the solid surface energy, as shown in Fig. 4. There is a surface energy of the liquid (\( \gamma_{lv} \)) representing the strength of the interaction or adhesive force between the liquid and the liquid, and a surface energy of the solid (\( \gamma_{sv} \)) representing the interaction or adhesive force between the liquid and the solid.
As shown in Figure 4, nonwetting occurs when the surface is high in liquid surface energy (liquid surface force and liquid cohesion) and low in solid surface energy (liquid and solid adhesive force). On the other hand, maximum wetting occurs when the surface is low in liquid surface energy and high in solid surface energy. Accordingly, the wettability of a surface depends on the correlation between the liquid and solid surface energy. Liquid surface energy is affected by intermolecular forces, while solid surface energy varies by two methods. The first method is physical that consist of increasing porosity and roughness (microstructures) of the surface, while the second is a chemical method where surface chemistry is modified [2].

*Figure 4 Relationship between surface energies and wettability of the surface.*
A variety of approaches have been proposed to control the wetting in different applications by tuning the liquid and solid surface energy. The use of oxides, for example, has been investigated with heat transfer to increase wetting speeds (and, therefore, increase the critical heat flux) in thermal management applications [2-4]. Moreover, external stimuli such as temperature [5-7], electricity [8-9], pH [10], and solvent [11] were used to modulate the wetting dynamics on various surfaces. For example, various methods have been reported to improve the controllable wettability of TiO$_2$-derived materials and their applications [12]. There have also been considerable attempts to tune the wettability with OPC (changing the surface chemistry of target surface) using Azobenzene [13-19], Spiropyran (SP) [20-22], and Donor-Acceptor Stenhouse Adducts (DASA) [23].

Photoswitching the wettability with light is advantageous because it is abundant and inexpensive. Moreover, using light, the wavelength, power, and spatiotemporal characteristics can be easily tuned. Among the OPCs, SP is one of the most used compounds which has been attached to polymers, biomacromolecules, and inorganic nanoparticle surfaces [24,25].

The main goal of this research is to study the wetting behavior of SP functionalized to Au on both flat (smooth) and microstructured surfaces. This method involves modulating the surface chemistry through light, which can change the surface energy and wetting behavior of the photoswitchable gold (SP conjugated to the gold surface via SAM linker (SP-SAM)). This study provides preliminary results for designing microstructured surfaces with tunable surface free energy perturbations via the photoisomerization of SPCOOH surface coatings.
1.3 Modulating the conductivity of polyaniline using Metastable-State Photoacid (mPAH)

In 2011, Liao introduced a new generation of OPCs which is called Metastable-State Photoacid (mPAH) [26]. Advantages of these compound was that they undergo reversible structural transformation upon irradiation of low energy visible light. The use of low-energy irradiation prevents the onset of photofatigue (the problem that occurs with SP in the presence of high energy radiation). mPAH can be classified in two types: merocyanine and trimethyl-phenyl-dihy-tricyanodrofuran. The merocyanine mPAHs, which are the compound of interest in this research, are composed of electron-accepting (EA) and nucleophilic (NuH) moieties linked by a double bond (Fig. 5). A visible light irradiation induces a trans-cis isomerization of the double bond. This enables a nucleophilic cyclization reaction to occur between these two moieties and releases a proton as a result (the mPAH is converted to a strong acid when exposed to visible light. In contrast, in the dark, the metastable form returns to its original form and absorbs the proton (Figure 5(b)).
In chapter 3, mPAHs were used to control the electrical conductivity of polyaniline (PANI). In this regard, new photoswitchable conductive film which consists of an mPAH visible light-sensitive mixture (contain of PVC, plasticizer, and cyclohexanone) drop casted on a flexible PET substrate precoated with a PANI-ES layer. The precoating of PET with PANI-ES layer converts it to a conductive flexible substrate. Thus, the conductivity of the film can be modulated upon irradiation with visible light, in a simple and inexpensive way.
1.4 References


CHAPTER 2 TUNING THE FLUID WETTING DYNAMICS ON GOLD MICROSTRUCTURES USING PHOTOACTIVE COMPOUNDS

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2.1 Abstract

Over the past few decades, different approaches have been taken to optimize surface wetting for various applications, including the surface engineering of different surface chemistries and surface micro- and nano-structures. This work demonstrates how photoactive compounds can be used to tune the surface chemistry, surface free energy, and the wetting velocity of fluids on Spiropyran functionalized surfaces with different surface microstructures. Evidence of this photowetting effect is based on data showing: (1) the cyclic changes in the static, advancing, and receding contact angles $\theta_{CA}$ for multiple UV$\leftrightarrow$vis photoswitching cycles with both smooth and microstructured surfaces and (2) the changes in the fluid wicking velocity (via UV$\leftrightarrow$vis photoswitching) on different Spiropyran functionalized hemiwicking surfaces. X-ray photoelectron spectroscopy is used to determine the efficiency of photoswitching caused by the quality of the Spiropyran functionalization. Reversible photoisomerization of Spiropyran generates a gradient in surface free energy, resulting in a similar change in contact angle ($\theta_{CA}$) in the photoswitchable surfaces. By incorporating these changes into the Owens-Wendt and Van Oss
surface energy models, the energy of smooth Au surfaces can also be predicted for both UV and visible light irradiations, where reversible contact angle variations of $\Delta \theta_{CA} \approx 5\text{--}10^\circ$ are achieved with both water and water-ethanol mixtures due to the conversion of SP to merocyanine, which corresponds to a total free energy change of $\sim 13\%$ on the photoswitchable surface.

**Keywords:** surface chemistry, surface wetting, microstructured surfaces, photoreactive compounds, hemiwicking

### 2.2 Introduction

Researchers have studied the dynamics of surface wetting over the past century to better understand the interaction between liquids and solids [1-2]. Studying these interactions is essential for a variety of applications, ranging from biomedical devices to self-cleaning surfaces [3-4]. The contact angle ($\theta_{CA}$) is a parameter commonly used to characterize the wetting behavior and the energetics of the solid/liquid interface (Fig. 1). Numerous attempts have been made to model the wetting behavior using $\theta_{CA}$, most famously through the Young-Dupree Equation [5-6]:

$$\cos \theta_{Eq} = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$  \hspace{1cm} (1)

Where $\theta_{Eq}$ represents the static or equilibrium contact angle and $\gamma_{lv}$, $\gamma_{sv}$ and $\gamma_{sl}$ are the liquid–vapor, solid–vapor, and solid–liquid interfacial surface energies, respectively [6]. It is worth mentioning that the surface free energy ($\gamma$) and surface tension ($\sigma$) were related by Shuttleworth [7] through the following equation:

$$\sigma = \gamma + A \frac{d\gamma}{dA}$$  \hspace{1cm} (2)
Where \( A \) is surface area, \( \sigma \) is the surface tension, and \( \gamma \) is the interfacial or surface Helmholtz free energy per unit area. For a one-component fluid, the \( d\gamma/dA \) term is negligible and, in result, \( \gamma \) and \( \sigma \) are often assumed to be equivalent - which is not necessarily accurate, especially for solids.

The magnitude of \( \theta_{CA} \) is most commonly used to describe the lyophilicity \( (\theta_{Eq} < 90) \) or lyophobicity \( (\theta_{Eq} > 90) \) of a surface material. With respect to aqueous fluids [8-10], the degree of hydrophilicity or hydrophobicity is then subsequently used to predict if a surface material is suitable for aqueous self-wetting or self-cleaning applications, respectively. Fig. 6 (a) shows the schematic of a water droplet on a hydrophobic surface. The wetting behavior of a surface can also be tuned by surface texturing with micro- to nano-scale surface structures [11-13]. To create a self-drying surface, microstructures are used to increase the hydrophobicity of a naturally hydrophobic surface [14]. Similarly, microstructures can also be used to increase the hydrophilicity of a naturally hydrophilic surface to create a self-wetting surface [15]. Fig. 6 (b) – (d) illustrate three key fluid wetting behaviors with microstructured surfaces. A Cassie-Baxter state (Fig. 6 (b)) occurs when the microstructures of a hydrophobic surface material prevent a fluid from wetting the entire surface. For example, the hydrophobic nature of the surface chemistry and the gradient of surface energy created by the air pockets in the microstructure array will prevent the liquid from reaching/wetting the substrate. Instead, the liquid will only rest on top of the microstructures [16]. The Wenzel state (Fig. 6 (c)) describes a condition where the liquid rests within the microstructure array as a droplet but does not spread throughout it. This state can occur for both hydrophobic and hydrophilic surfaces [17]. Lastly, the hemiwicking state (Fig. 6 (d)) describes the movement (wicking) of fluid through the surface textures of a hydrophilic surface material induced by a
cascading, capillary force effect with each microstructure (i.e., each micropillar acts as a fluid pump and a fluid droplet can wet a surface beyond its equilibrium wetting length). Some common applications for hemiwicking include thermal control systems, such as heat pipes [18].

![Diagram](image)

**Figure 6** A representation of the interfacial forces forming the contact angle of a fluid on (a) a flat hydrophobic surface and (b-d) microstructured surfaces for the Cassie-Baxter, Wenzel, and Hemiwicking wetting states, respectively. The contact angles depicted for the (b) Cassie-Baxter and (c) Wenzel states are the apparent contact angles for the textured surface, where $\theta_{CB} > \theta_W > \theta_{Eq}$ and $\theta_{Eq}$ are the contact angles for the flat (non-textured) surface region.

While multiple research groups have demonstrated systems that can exhibit wetting transitions between the Wenzel and Cassie-Baxter states [19-21], an active tuning between the static Wenzel (or Cassie-Baxter) state to the dynamic hemiwicking state has yet to be demonstrated. It is important to note that the difference in static and dynamic wetting characteristics are dependent on multiple parameters, including the advancing and receding contact angles, the geometry of the surface texture, the presence of surface energy gradients (intrinsic
and/or induced), and absorption kinetics. Nevertheless, the ability to actively switch between the Cassie-Baxter, Wenzel, and Hemiwicking states will lead to transformative fluidic (heat pipe) technologies – especially if the wetting state transitions can be controlled by contact-free stimulants such as light.

A variety of approaches have been proposed to control the wetting dynamics in different applications by tuning the interfacial properties both actively and passively. The use of oxides, for example, has been investigated with nucleate heat transfer to increase wetting speeds (and, therefore, increase the critical heat flux) in thermal management applications [22-24]. Moreover, external stimuli such as temperature [25–27], electricity [28-29], pH [30], and solvent [31] were used to modulate the wetting dynamics on various surfaces. For example, various methods have been reported to improve the controllable wettability of TiO$_2$-derived materials and their applications [32]. There have also been considerable attempts to tune the wettability with organic photochromic compounds (OPC) toward photoswitchable surfaces (Azobenzene [33-39], Spiropyran (SP) [40-42], and Donor-Acceptor Stenhouse Adducts (DASA)) [43].

OPCs are a class of photoactive compounds that undergo reversible structural transformation of their physicochemical properties (i.e., polarity and charge distribution) upon light irradiation (photoisomerization) as an external stimulus [44,45] For passive applications, photoswitching with light is advantageous because it is abundant and inexpensive. Moreover, for active applications, the wavelength, power, and spatiotemporal characteristics can be easily tuned. Among the OPCs, SP is one of the most used compounds and it has been attached to polymers, biomacromolecules, and inorganic nanoparticle surfaces [46,47]. In this study, carboxylated SP
was used to conjugate to the Au on both a flat (smooth) surface as well as a microstructured surface. A different type of OPC was also investigated. We attempted to apply DASA (Donor-Acceptor Stenhouse Adducts), which is a visible light activated compound, but this approach failed.

The main goal of this research is to study the wetting behavior of SP functionalized to Au on both flat (smooth) and microstructured surfaces. The variations in the static and dynamic (advancing and receding) contact angles are analyzed with both smooth and microstructured surfaces to access the possibility of reversible switching between the static Cassie-Baxter (or Wenzel) state and the dynamic hemiwicking state. Moreover, the wetting behaviors of multiple fluids with varying polarity (ethanol-water mixtures) are studied. Based on the variation in surface free energy, these changes are measured for water, ethanol, and binary water/ethanol mixtures. The surface chemistry is modulated by irradiation of light, which can alter the surface energy and wetting behavior of the photoswitchable Au (SP-SAM). The study provides preliminary results for designing microstructured surfaces with tunable surface free energy perturbations via the photoisomerization of SPCOOH surface coatings.

2.3 Experimental setup

2.3.1 Synthesis of SPCOOH

The synthesis of SPCOOH consists of two steps. In the first step, we proposed a new synthesis method for 1-(2-carboxyethyl)-2,3,3-trimethyl-3H-indolium bromide, which functions as a SPCOOH precursor. In the second step, SPCOOH is synthesized by modifying a literature procedure (Fig. 14-16).
2.3.2 Creating the microstructured surface

The change in the wetting behavior is analyzed from contact angle experiments with both flat (smooth) Au and microstructured Au sample substrates. Commercially available flat Au substrates were obtained from Infolab, Inc. Two methods were used to fabricate Microstructured Au substrates. The first method was used in our previous work to obtain a microstructured substrate in a timely and cost-effective manner employing a negative mold application [48]. A microstructured surface is created after the polydimethylsiloxane (PDMS), Norland optical adhesive 61 (NOA), or JB-Weld has been cured on the plastic mold. DC magnetron sputtering is used to deposit a ~100 nm thick, thin film of Au on the soft material samples. The second method involves polymerization using a Nanoscribe Pro GT laser lithography system to fabricate microstructures on a silicon wafer (thickness = 0.5 mm). The microstructures are then coated with a thin, protective layer of Al₂O₃ (~150 nm) to maximize robustness and surface energy uniformity. These microstructured samples (or anisotropic hemiwick arrays) were fabricated at the Center for Nanophase Material Sciences at Oak Ridge National Laboratory (ORNL). Then, ~100 nm of Au was deposited on the Al₂O₃ coating (via DC magnetron sputtering). Table 1 provides a summary of the geometries of the microstructured wicking arrays used in this study.
Table 1 Pillar packing orientation, shape, geometry (base diameter $d$, height $h$, spacing $s_x$, skew $\alpha$, slant $\beta$ angle), and roughness factor $f_r$ of the microstructured hemiwick ing samples used in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Orientation</th>
<th>Shape</th>
<th>$d$ (µm)</th>
<th>$h$ (µm)</th>
<th>$s_x$ (µm)</th>
<th>$\alpha$ (deg)</th>
<th>$\beta$ (deg)</th>
<th>$f_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Staggered</td>
<td>half-Cylinder</td>
<td>20</td>
<td>17.5</td>
<td>40</td>
<td>45</td>
<td>0</td>
<td>1.28</td>
</tr>
<tr>
<td>2</td>
<td>Cubic</td>
<td>Crescent</td>
<td>20</td>
<td>20</td>
<td>50</td>
<td>0</td>
<td>0</td>
<td>1.46</td>
</tr>
<tr>
<td>3</td>
<td>Cubic</td>
<td>half-Cylinder</td>
<td>30</td>
<td>25</td>
<td>50</td>
<td>0</td>
<td>0</td>
<td>1.77</td>
</tr>
<tr>
<td>H</td>
<td>Cubic</td>
<td>half-Conical</td>
<td>20</td>
<td>44</td>
<td>50</td>
<td>0</td>
<td>12.8</td>
<td>1.46</td>
</tr>
<tr>
<td>G</td>
<td>Staggered</td>
<td>half-Conical</td>
<td>30</td>
<td>97</td>
<td>40</td>
<td>45</td>
<td>8.8</td>
<td>2.18</td>
</tr>
<tr>
<td>K</td>
<td>Cubic</td>
<td>half-Conical</td>
<td>30</td>
<td>58</td>
<td>50</td>
<td>0</td>
<td>14.5</td>
<td>1.91</td>
</tr>
</tbody>
</table>

2.3.3 Fabrication of photoswitchable surfaces

Fig. 7 illustrates the two steps required to prepare SP functionalized surfaces on both the flat and microstructured Au sample substrates. Initially, the Au substrate is immersed in a 5mM solution of cystamine dihydrochloride for 48 hours to produce a self-assembled monolayer (SAM) containing a terminal amino group. The SAM functionalized Au is then rinsed with DI water and placed in an ethanolic solution containing 5 mM carboxylated SP (SPCOOH) and 1 mM 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and left in the solution overnight. EDC acts as a coupling agent to facilitate the formation of amides from amines and carboxylic acids. A condensation reaction occurs between the amino groups of cystamine and the carboxylic acid groups of SPCOOH, resulting in an SP-functionalized Au surface (SP-SAM). The surface chemistry of SAM and SP-SAM attached to the Au surface was analyzed using X-ray photoelectron spectroscopy (XPS). The XPS experiments were conducted using a Physical Electronics 5400 Electron and Spectroscopy for Chemical Analysis (ESCA).
Figure 7 The process for (a) functionalization of cystamine and SPCOOH onto an Au substrate (b) photoisomerization of SP on the Au substrate increase the polarity of the surface.

2.3.4. Photoswitching experiments

The photoswitchable Au substrate undergoes a ring opening of SP (MC) with UV light irradiation and switches back to the closed form of SP with visible light irradiation (Fig. 7 (b)). The ring opening of SP produces positive charges in nitrogen and negative charges in oxygen. UV-AC Hand Lamps ($\lambda = 365$ nm) and a 120 LED array ($\lambda = 520$ nm) were used to induce the ring opening and closing of SP, respectively. The wavelength at which SP is getting activated during the ring opening and ring closing reactions. In the UV region, we used two wavelengths of 254nm and 365nm to determine the optimal wavelength for opening the ring and two wavelengths in the Vis region, 470nm and 520nm, to determine the optimal wavelength for closing the ring. These
wavelengths were utilized for varying periods of time ranging from one to three minutes. The wavelengths were selected based on the absorption experiments with SPCOOH in ethanolic solution Fig. 17. Based on these experiments, one minute of UV irradiation is optimized for the photoisomerization of SP into merocyanine (MC) and ten minutes of visible irradiation for the reverse reaction (MC into SP). The photoswitching experiments were conducted in three cycles.

2.3.5. CA measurements

Fig. 8 illustrates the wetting experiment for photoswitchable surfaces measured by contact angle analysis using a VCA-Optima surface analysis (AST Products, Billerica, MA). Using a computer-controlled syringe pump, a droplet of 6 μL of water was dispensed on the surface and an image of the static droplet was captured. In addition to the static contact angle, the VCA instrument was used to measure the advancing and receding contact angles. The advancing angle was captured by placing a droplet on a surface and then adding fluid to the droplet (increasing its volume and contact angle), until the droplet’s contact angle “de-pins” from the surface and then advances along the surface to a value close to the droplet’s equilibrium contact angle. Thus, the advancing contact angle corresponds to the contact angle at the inception of "de-pinning". A similar method was used to capture the receding angle, but the syringe was used to remove fluid from the droplet (reducing its volume and contact angle) until de-pinning occurs. Video recordings capture the droplet dynamics for these advancing and receding experiments. The experiments were performed under a red-light lamp (λ ≈ 780 nm) since it does not affect the structure of SP as shown by the absorption plots in the Fig. 17. In between successive trials and other subsequent experiments, the samples were cleaned with DI water and dried with nitrogen gas.
Figure 8 (a) Schematic depiction of the surface wetting apparatus for measuring the advancing, receding, and static contact angles. (b) Schematic depiction of the vertical hemiwicking apparatus.

2.3.6. Hemiwicking

The hemiwicking experiments were performed on functionalized SP microstructures to determine the effects of wetting state transitions for different ‘light-induced’ variations in surface energy, changes in fluid composition, and variations in surface texture. A high-speed camera (Fig. 8(b)) was used to capture the hemiwicking dynamics of ethanol/water mixtures (25:75, 50:50 and 75:25 volume % of ethanol:water, respectively). The hemiwicking experiments investigated the both the ‘open’ and ‘closed’ SP-states. The 75:25 mixture has the smallest surface tension, making it more likely to wick while retaining its polarity. The presented data are based on vertical wicking experiments (against gravity) using a vertical translation stage (Fig. 8 (b)), where a solution reservoir was moved up to the hemiwicking sample until it met the first-row pillars in the hemwicking pillar array. The hemiwicking process starts at the onset of fluid meniscus contact with the pillar array. The wicking dynamics were captured at 100 frames per second (fps) at an image resolution of 14.71 μm/pixel. Similar to the contact angle experiments, after UV (\(\lambda = 365\) nm) or vis (\(\lambda = 520\) nm) light exposure, hemiwicking dynamics were monitored under a red-light
lamp ($\lambda \approx 780$ nm) for visual purposes since it does not affect the structure of SP. Horizontal wicking experiments from droplets (representative of Fig. 6 (d)) were also conducted. However, we did not observe UV$\leftrightarrow$vis photoswitching transitions between the hemiwickung state and the Wenzel (or Cassie-Baxter) states.

2.4 Results and discussion

2.4.1 Advancing, receding, and static CA with water

Fig. 9 shows the changes in the static and dynamic contact angles for water on the SP functionalized flat Au sample for three UV$\leftrightarrow$vis photoswitching cycles. With UV-light $\theta_{CA}$ decreases due to the photoisomerization of hydrophobic SP to hydrophilic MC (see Fig. 7 (b)). The static $\theta_{CA}$ changed by approximately 10 degrees, which is comparable to previous studies [33,37-40] and decreased over the second and third cycles due to SP photodegraded during exposure. In fact, Spiropyran photoisomerization is associated with some side reactions. These reactions can lead to by-products that lack the photoresponsive properties [46]. One of the most important mechanisms for these side reactions is due to the interaction of the long-lived triplet excited state of SP with the triplet oxygen ($^{3}$O$_2$). This generates a singlet oxygen ($^{1}$O$_2$) which initiates irreversible oxidation of the photoswitching process(photodegradation) [46].
Dynamic contact angles were also used to determine changes in the wetting dynamics in a non-equilibrium state. The dynamic (advancing and receding) contact angles are tied to $d\gamma/dA$ (Eq. (2)) and heterogeneities in surface energy. The advancing contact angle results in Fig. 9 show comparable switches in the magnitude of the static contact angle experiments, while the receding contact angle data show a lower degree of photoswitchability. Nevertheless, for all conditions (static and dynamic), the behavior of the photoswitching shows that changes in the surface chemistry result in variations in the solid/liquid interface (Fig. 18 and Table 1). It is worth mentioning that the changes in the advancing and receding angles reveal overall alterations in critical wetting dynamics that can be used in a variety of applications. For example, the switchability of the advancing angle indicates the variation of interfacial forces which can also
affect the ability of a surface to self-clean or wet a particular area, depending on the hydrophilicity of the surface.

2.4.2. Composition of photoswitchable surface

XPS was conducted to determine the composition of the SAM and SP-SAM on the switchable surface. Six spots were selected for XPS analysis in both measurements. The results are presented in Table 2 and Fig. 10.

Figure 10 XPS spectra after formation of (1) SAM (blue), (2) SP-SAM on a flat Au substrate.

Carbon is the most abundant element on the SP-SAM surface, followed by oxygen, nitrogen, and Au. The C 1s spectrum (binding energy ranging ~ 282–286 eV) is the result of the
formation of SAM using C-C: 284.8 eV, C-S bond: ~284.5, C-N: ~285.5, C-Cl: ~ 285.2, C-H~286 eV and formation of SP-SAM C-O-C: ~286 eV. The N 1s region (binding energy ~ 397–400 eV) shows the formation of SAM (peaks at ~ 399.5 and ~ 400.8 eV can be attributed to the N-H and N-C, respectively). The O 1s spectrum (binding energy ~ 529-533 eV) confirms the oxidation of both the SAM and SP-SAM surfaces. SAM induces oxidation of the thiol groups formed upon adsorption of cystamine. This process produces either SO₃⁻ ions or SO₂⁻ groups, which desorb from the Au surface. Furthermore, the oxidation can be caused by multiple factors, including prolonged immersion times, oxygen in the SAM solution, air exposure, and photooxidation of the photoswitchable surface by UV exposure [49]. Also, the oxidation process occurs during samples preparation for XPS as well as during the photoswitching experiment. Oxidation can decrease photoswitching on surfaces by washing out the SAM and SP-SAM with a polar solvent, such as water (during experiments) [50].

Table 2 Element composition on the Au surface

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
<th>SAM</th>
<th>Photoswitchable surface (SP-SAM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C, 1s</td>
<td>52.82</td>
<td>66.54</td>
<td></td>
</tr>
<tr>
<td>O, 1s</td>
<td>12.68</td>
<td>14.2</td>
<td></td>
</tr>
<tr>
<td>N, 1s</td>
<td>3.1</td>
<td>9.18</td>
<td></td>
</tr>
<tr>
<td>Au, 4f</td>
<td>28.8</td>
<td>8.05</td>
<td></td>
</tr>
<tr>
<td>S, 2p</td>
<td>2.6</td>
<td>2.03</td>
<td></td>
</tr>
</tbody>
</table>

Quality control of SAM and SP-SAM is imperative to increase the overall performance of photoswitchable surfaces. Highly aligned SAMs, theoretically, can contain higher terminal amino group packing densities. The ideal carbon to nitrogen molar ratio is [C/N] ~2, maximizing the possibility of a condensation reaction between the terminal amino atom of SAM and the carboxylic
acid group of SPCOOH. Thus, ideal alignment results in a higher density of SP-SAM on the surface. As shown in Table 2, the SAM carbon to nitrogen molar ratio is [C/N] ~17 (~ 8 times greater than the theoretical value of 2), which suggests that either the fabricated SAM is not well aligned or there is airborne molecular contamination (adventitious carbon) [50,51]. The lack of surface coverage and non-ideal alignment are presumably the primary causes of a partially covered and misaligned SAM. A partially covered and misaligned SAM is likely to be caused by a lack of surface coverage and non-ideal alignment in the gold and bulky SP groups.

Several important factors contribute to the formation of SAM, such as immersion time and cystamine concentration in the SAM solution [52,53]. The SAM in the photoswitchable surface was formed by immersing the Au substrate in 5mM cystamine dihydrochloride solution over 48 hours (1-10 mM and 1-24 h are prevalent ranges for SAM formation [54-56]). Results showed that 5 mM of cystamine dihydrochloride provides superior photoswitching in comparison to a higher concentration of 7.5 mM (Fig. 19). Extended immersion times have a contradictory effect. On the one side, increasing surface coverage of SAMs results in fewer defects. On the other side, prolonged immersion times are associated with an increase in the amount of oxidized carbon and sulfur in the photoswitchable surface [50]. The 12.68% of the oxygen in the SAM is composed mainly of oxidized carbon and sulfur. Oxidized sulfur may result in the detachment of the SAM from the Au surface and a decrease in the switching performance.

Besides the SAM, the SP-SAM structure and quality have an important impact on the wetting behavior of the photoswitchable surface. First, the SP-SAM quality is reduced by the presence of bulky SP groups in the formation procedure. Sterically bulky SPs inhibit the
development of densely packed SP-SAMs and result in a disordered SAM [50]. Second, the
formation reaction of SP-SAM is incomplete (amino groups in the 398-400 eV region of the XPS
spectrum (Fig. 10)). This reduces the number of attached SP to the Au and consequently its
photoswitching performance. And finally, photodegradation of SP upon UV irradiation leads to a
decrease in $\Delta \theta_{CA}$ after repeated UV$\leftrightarrow$vis photoswitching cycles (see Sec. 3.1).

2.4.3. Results of ethanol-water mixture and Surface Energy Analysis

The free surface energy variation between the ‘open’ and ‘closed’ form of SP is due to the
different types and magnitudes of intermolecular interactions [57]. This variation mainly comes
through the exposure of the positive and negative charges in the open state (i.e., after UV light
exposure) and the structure with no free charges in the closed state (i.e., after visible light
exposure). For this study, the Owens-Wendt and the Van Oss Chaudhury Good models were used
to predict the surface energy variations of the photoswitchable surface upon UV or vis light
irradiation. These two surface energy models consider the polar and nonpolar contributions of the
liquid and the solid surface to predict the contact angle. The Owens-Wendt, which is closely related
to Fowke’s Theory, can be expressed through the following equation [58]:

$$\frac{1+\cos \theta_{CA}}{2} \frac{\gamma_l}{\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^p \gamma_l^d} \gamma_s^d + \sqrt{\gamma_s^d},$$

(3)

Where $\gamma_l$ is the surface energy of the fluid, $\gamma_s$ is the solid surface energy, $\gamma^p$ is the polar
component of the surface energy, and $\gamma^d$ is the non-polar component of the surface energy. The
Van Oss Chaudhury Good model, or simply Van Oss model, analyzes the wetting through two
different aspects of the polar surface energy, the electron accepting (acid, $\gamma^+$) and the electron
donating (base, $\gamma^-$) components. In relation to the polar component of surface energy, the acid and
base contributions are given by the following equation [58]:

$$\gamma^p = 2\sqrt{\gamma^+\gamma^-}$$  \hspace{1cm} (4)

Using this contribution, the Van Oss model calculates surface wetting using [59]:

$$(1 + \cos \theta_{CA})\gamma_t = 2 \left(\sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^+ \gamma_l^-} + \sqrt{\gamma_s^- \gamma_l^+}\right)$$ \hspace{1cm} (5)

Data from the ethanol and water experiments can be used to find the surface energy
components using both the Owens-Wendt and Van Oss models. A proper application of the Van
Oss model requires, however, an estimate of the surface energy. An approximation for the total
surface energy is provided through the Chimbowski method, which is presented in the following
[60]:

$$\gamma_s = \Pi \frac{(1+\cos \theta_{adv})^2}{(1+\cos \theta_{rec})^2-(1+\cos \theta_{adv})^2}$$ \hspace{1cm} (6)

Where $\Pi$ is the film pressure between the thin, absorbed film layer of a fluid and the
surface. $\Pi$ can be calculated using the following equation:

$$\Pi = \sigma (\cos \theta_{rec} - \cos \theta_{adv})$$ \hspace{1cm} (7)
The data from the dynamic contact angle experiments with water are used to find the solid surface energy. The polar and non-polar components of the surface energy are then related through the following equation [61]:

$$\gamma = \gamma^p + \gamma^d$$  \hspace{1cm} (8)

Equations (1-9) are then used to calculate the changes in the surface free energy based on the wetting data gathered for both water and ethanol. To verify the surface energy values, both the theoretical and experimental contact angles of the ethanol/water mixtures are compared at different volume fractions \(\phi\) (for both the ‘open’ and ‘closed’ forms of SP on the photoswitchable surface). The surface energy of the fluid mixtures for the Owens-Wendt and Van Oss models are estimated using effective medium theory (EMT), see Eq. (7). Additional details regarding the properties of the fluid mixtures are provided Figs. 20 and 21.

$$\sigma_{mix} = \sum_1^N \phi_i \sigma_i$$  \hspace{1cm} (9)
Table 3 Surface energy components for water, ethanol, and the photoswitchable SP functionalized Au surface, using the Owens-Wendt and Van Oss Models [58-64] for the UV light ('open') and vis light ('closed') photoswitching states.

<table>
<thead>
<tr>
<th>Material</th>
<th>( \sigma^* ) (mN/m)</th>
<th>( \gamma^d ) (mN/m)</th>
<th>( \gamma^p ) (mN/m)</th>
<th>( \gamma^+ ) (mN/m)</th>
<th>( \gamma^- ) (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.8*</td>
<td>21.8</td>
<td>51</td>
<td>25.5</td>
<td>25.5</td>
</tr>
<tr>
<td>Ethanol</td>
<td>23.2*</td>
<td>21.4</td>
<td>1.8</td>
<td>0.09</td>
<td>9.0</td>
</tr>
<tr>
<td>SP-Au, Closed (vis), Owens-Wendt</td>
<td>31.14</td>
<td>9.51</td>
<td>21.63</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SP-Au, Open (UV), Owens-Wendt</td>
<td>34.79</td>
<td>8.40</td>
<td>26.39</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SP-Au, Closed (vis), Van Oss</td>
<td>29.84</td>
<td>8.96</td>
<td>20.88</td>
<td>7.27</td>
<td>14.99</td>
</tr>
<tr>
<td>SP-Au, Open (UV), Van Oss</td>
<td>33.67</td>
<td>7.34</td>
<td>26.34</td>
<td>9.13</td>
<td>19.00</td>
</tr>
</tbody>
</table>

Figure 11 Comparison of the theoretical and experimental contact angles for water, ethanol, and water/ethanol mixtures using (a) the Owens-Wendt (Eq. (1)) and the Van Oss (Eq. (3)) wetting models and (b) variations in the water volume fraction derived from the Van Oss model.

Table 3 provides our results for the different surface free energy contributions. Using these calculated surface energy values, Fig. 11 then summarizes our results in terms of \( \theta_{CA} \) measured.
and $\theta_{CA}$ predicted based on the different surface free energy contributions provided in Table 3. Despite minor differences in the surface energy values, both models can approximate the value of the surface energy and its overall changes rather well. Moreover, as illustrated in Fig. 12, the experimental results for pure ethanol ($\phi = 0$) and pure water ($\phi = 1$) were rather accurate for predicting $\theta_{CA}$ of the water/ethanol mixtures. According to the Van Oss model, there is a 12.84% increase in the total free surface energy upon photoisomerization of closed form SP state to the open form MC state. Thus, both the experiment results and the surface energy modeling indicate that the overall increase in free surface energy is primarily due to an increase in the polar surface energy component - which is caused by the presence of the positive and negative charges in the open (MC) state. These finding also support that the surface charge (polarity) causes the primary changes in the surface free energy - resulting in the expected overall change in the wetting behavior (or $\theta_{CA}$ as a function of the UV$\leftrightarrow$vis light stimulation).

The Van Oss model can provide a better understanding of the changes in the polar component of the surface energy. As mentioned earlier, the Owens-Wendt model only considers the total polar component of surface energy, while the Van Oss model analyzes the acid-base component of surface tension. Positive and negative charges exposed in the ‘open’ SP state are representative of the nitrogen and oxygen molecules, respectively (see Fig. 7 (b)). Based on the Van Oss models, it is observed that the main changes in the polar component of the surface energy are caused by the electron donating (i.e., base) component. This indicates that the negative charges on oxygen molecules in the ‘open’ SP state are more influential in altering the overall surface tension than the positive charges on nitrogen molecules.
2.4.4. The impact of Surface Microstructure

2.4.4.1 Cassie-Baxter, Wenzel, and Hemiwicking State

Fig. 12 shows the measured changes in $\theta_{CA}$ for three UV$\leftrightarrow$vis irradiation cycles for two different photoswitchable surfaces. Similar to the $\Delta \theta_{CA}^{UV\leftrightarrow vis}$ modulations observed for the smooth (flat) SP-functionalized Au surface, the apparent $\theta_{CA}$ for the microstructured pillar array varies depending on the SP state of the photoactive compound. Thus, photoisomerization of the SP state to MC state not only alters the intrinsic surface free energy of the functionalized Au surface, but also modulates the capillary force coupled to the surface texture of the microstructure. The hypothesis here was observing the contact angle variation exceeding 10 degrees, as a result of the photoisomerization of the photoactive compound [34,36]. While the photoactive compound only facilitates relatively small modulations in $\theta_{CA}$ (~5-10°), the tunability of $\theta_{CA}$ is repeatable and still offers preliminary results towards the design of systems that can exhibit this photowetting effect with both textured and non-textured surfaces. Moreover, these results support the broader impacts of potentially using other OPCs for tunable wetting beyond that for flat surfaces, where the wetting dynamics can be controlled/tuned by engineering both the surface microstructure and the surface photochemistry.

Multiple researchers have derived criterion for predicting the different wetting states and wetting state transitions [65-70]. Most commonly conventional wetting theory [67] is used, where it can predict the apparent contact angle for all three wetting states based on the geometry of the surface microstructure, the fractional wetted area, and the equilibrium contact angle of the intrinsic surface material without microstructures. For the Wenzel state (Fig. 6 c), conventional theory
predicts the apparent Wenzel state contact angle ($\theta_W$) to follow as $\cos \theta_W = f_r \cos \theta_{CA}^*$, where $\theta_{CA}^*$ represents the equilibrium contact angle for the non-textured (flat) surface and $f_r$ is the roughness factor (i.e., the ratio of the total surface area of the microstructured surface to the projected surface area). On the other hand, the apparent Cassie-Baxter contact angle ($\theta_{CB}$) for the traditional, air-pocket wetting regime (Fig. 6 b) can be expressed as $\cos \theta_{CB} = \Phi (\cos \theta_{CA}^* + 1) - 1$, where $\Phi$ is the fraction of the wetted solid surface area to the projected surface area. Based on these wetting state predictions, the photo-induced changes in $\theta_{CA}$ for water with microstructured sample in Fig. 12a corresponds to slight perturbations in an unstable Cassie-Baxter wetting state with $98^\circ \lesssim \theta_{CB} \lesssim 108^\circ$, using $\Phi \approx 0.5$-$0.7$ and $\theta_{CA}^* \approx 67$-$85^\circ$ based on the bare Au photoswitching results. Therefore, with further enhancements in the photoisomerization of the SP surface coating, a Cassie-Baxter to Hemiwicking (or droplet penetration) state transition is feasible. For example, if UV light stimulation can reduce the apparent Cassie-Baxter contact angle with water to the hydrophilic state (i.e., $\theta_{CB} \leq 90^\circ$), then the Cassie-Baxter to Hemiwicking state transition should occur via a cascading Cassie-Baxter to Wenzel to hemiwicking transition. Equivalently, reversible Cassie-Baxter to Hemiwicking transitions are expected with water if $\text{UV} \rightleftharpoons \text{vis}$ stimulation can induce the corresponding intrinsic contact angle conditions: $\theta_{CA}^{\text{UV}} \leq 40^\circ$ and $\theta_{CA}^{\text{vis}} \geq 90^\circ$. This $\Delta \theta_{CA}^{\text{UV} \rightleftharpoons \text{vis}} \geq 50^\circ$ criterion is significantly greater than the $\sim$5-10$^\circ$ variations observed. Yet, these estimates are potentially overestimates because $\Phi$ is also influenced by the light induced changes in surface energy. Nevertheless, these estimates are supported by recent wetting state predictions by others - see, e.g., Fig. 2e in [70].
Figure 12 The effects of SPCOOH functionalization, surface microstructure, and UV-vis photoswitching on the static contact angle. (a) Contact angle data for water droplets on both bare (smooth) Au and microstructured Au surfaces before and after SPCOOH-functionalization and then with subsequent UV-vis photoisomerization of the SP surface coating. (b) Contact angle data for different water-ethanol mixtures. The circle symbols (○) represent equilibrium contact angles for water (or water-ethanol mixtures) on the smooth (non-textured) Au surface, whereas the triangle symbols (△) represent the apparent contact angles for a microstructured sample surface - (a) Sample-3 and (b) Sample-2 (see Table 1). The initial (no SPCOOH) data points correspond to the contact angles measured with the untreated Au surface (i.e., before the Au surface was functionalized with the photoactive SPCOOH compound). The data are based on multiple experiments (5 minimum per data point), where (a) provides data for multiple trials.

2.4.4.2. Hemiwicking Results

Along with tracking observable changes in the Cassie-Baster or Wenzel state, changes in the hemiwicking performance were also recorded. The results of our hemiwicking experiments are presented in Fig. 13. The changes in the hemiwicking performance were tracked by measuring the distance traveled by the leading edge of the wicking front as a function of time. The results indicate that, similar to what was observed with the Wenzel state, the photoisomerization of the SP will
enhance the hemiwickung performance on the microstructured surfaces. For these experiments, a 75:25 ethanol-water mixture was used. Hemiwickung and hemiwickung enhancements with the tested wicking arrays are not possible with pure water because $\theta_{CA}^{H_2O} \gg \theta_{CA}^{Zipping}$ [64,71].

Figure 13 Hemiwickung enhancements by UV light stimulation for a 75:25 ($\phi=0.75$) ethanol/water fluid mixture on different wicking structures (SP functionalized). (a) Effects of UV and Vis light stimulation on the vertical hemiwickung performance for different anisotropic (half-conical) SP functionalized microstructured surfaces. The results are plotted in terms of the squared distance ($L^2$) traveled by the fluid's meniscus front as a function of time ($t$). The closed and open symbols represent the rapid ascent (RA) and sluggish climb (SC) wicking orientations, respectively. (b) Corresponding UV enhanced hemiwickung performance in terms of the interfacial diffusivity ratio ($D_t^{UV}/D_t^{vis}$) as a function of the predicted solid-liquid Structure factor $S$ (evaluated at both the midpoint ($L=2.5$ mm) and the end ($L=5$ mm) of the wicking arrays). The inset image in (b) also depicts the corresponding pillar geometry orientation for SC and RA hemiwickung.

To emphasize the diffusive nature of the hemiwickung process, we plot the data in terms of the interface diffusivity $D_t$ of the wicking front:

$$L \sim (D_t t)^{1/2}$$

(10)
Where $L$ is the distance traveled by the wicking fluid, $D_I$ is the interface diffusivity, and $t$ is the time of travel. These results show that the dynamic surface wetting is impacted by the change in surface chemistry (or energy) due to photoisomerization. Thus, the orientation of the SP impacts both the static and dynamic surface wetting behavior. Based on these UV$\leftrightarrow$vis hemiwicking results, it is clear that the use of photoreactive compounds can dictate the wicking speeds in-real time beyond what can be achieved by changes in the surface structure alone.

Recent work on hemiwicking has derived a solution for the hemiwicking velocity in compact form as [72-74]:

$$U(L) = \frac{1}{C_{d0}} \left( \frac{\sigma}{\mu} \right) S = \frac{1}{C_{d0}} \left( \frac{\sigma}{\mu} \right) \frac{K}{L}$$

Where $U$ is the hemiwicking velocity, $C_{d0} \approx 24$ is the drag coefficient in the Stokes flow regime ($Re \ll 1$), $S = K/L$ is the dimensionless solid-liquid Structure factor, $K$ is the solid-liquid surface texture, and the surface tension to dynamic viscosity ratio $(\sigma/\mu)$ is a capillary velocity (which represents the maximum speed for wetting a flat, dry surface). Based on equations (10-11) the interface diffusivity of the propagating meniscus front is predicted as: $D_I = \frac{2}{C_{d0}} \left( \frac{\sigma}{\mu} \right) K$. The solid-liquid Structure factor $S$ ties the surface chemistries of the fluid and solid (i.e., the attractive solid-liquid interfacial forces) with the surface microstructure. Thus, both solid-liquid Structure factor ($S$) and the solid-liquid surface texture ($K$) couple the fluid-solid wetting behavior to the geometry/texture of the hemiwicking surface.
Past work derived the wicking/pumping force per unit wicking cell width ($f_w \approx \sigma \kappa \frac{A_w}{s_y}$) based on a liquid meniscus curvature scaling as $\kappa \sim h/x_0^2$, where $h$ is the pillar height and $x_0$ is the measured, steady-state meniscus extension. For this work we revisited the wicking/pumping force per unit cell width based on the contemporary capillary rise problem with a meniscus curvature scaling as $\kappa \sim 2 \cos(\theta_{CA}^* + \beta) / s_\kappa$, where $\beta$ is the slant angle of the pillar walls relative to the substrate surface normal and $s_\kappa$ is the interpillar gap separation (see Fig. 22). As a result, a force balance between the viscous drag and wicking force ($f_w \approx f_{C_{d0}}$) leads to the generalized solution for the solid-liquid surface texture,

$$K = \frac{2 \cos(\theta_{CA}^* + \beta)}{s_\kappa} \left[ \frac{A_w}{A_{C_{d0}}} \right] L_C \left( \frac{s_x}{\cos \alpha} - d^* \right) \quad (12)$$

Where $\theta_{CA}^*$ is the equilibrium contact angle of the fluid meniscus in contact with the pillar wall, $\frac{A_w}{A_{C_{d0}}}$ is the ratio of the pillar surface area for pumping/wicking to drag per unit cell, $L_C$ is the characteristic length for the flow-field ($\text{Re} = \rho UL_C / \mu$), and the $(s_x / \cos \alpha - d^*)$ term accounts for packed bed limit with $d^* = d$ for cylindrical pillars. Thus, the revised wicking model accounts for light-activated changes in the wetting behavior ($\theta_{CA}^{\text{UV\leftrightarrowvis}}$) and anisotropic pillar geometries ($\beta \neq 0$). We note that $\theta_{CA}^*$ used in the wicking model should be that of the flat wall (or that relative to the surface normal of pillar wall), not the apparent contact angle of the fluid with the microstructured surface.

The revised hemiwicking model is supported by a majority of acquired UV\leftrightarrowvis hemiwicking data (Fig. 13), where, in general, the vertical hemiwicking velocities (or diffusivity
of meniscus interface) increases upon UV photoisomerization of the open-SP surface state. Therefore, along with the static pillar geometry and pillar spacing configuration, the dynamic state of the surface chemistry is a key metric for engineering the wetting behavior. Such transient surface-chemistry effects are crucial in areas such as thermal transport, where the real-time changes in surface chemistry (via surface oxidation and fouling at high heat fluxes) result in significant, irreversible reductions in the nucleate boiling heat transfer coefficients and critical heat flux properties.

Our choice of the tested (vertical) wicking orientation is also worth clarification - i.e., vertical hemiwicking from a fluid pool as opposed to lateral hemiwicking from a droplet (or fluid penetration). We did test both wicking configurations. However, while we did observe UV↔vis photoswitching of the apparent contact angles with multiple fluids (Fig. 12), we did not observe Wenzel (or Cassie-Baxter) to hemiwicking state transitions with the presented fluid droplets on the photoactive microstructured surfaces. Therefore, the final studies focused on vertical hemiwicking against gravity from a fluid pool to demonstrate tunability of the wicking force via photoisomerization of SP on microstructured Au substrates. In regard to the propagation dynamics of the hemiwicking front, while we were able to modulate the static and dynamic contact angle over a relatively broad range using water and ethanol-water mixtures, we did not observe significant and reproducible variations in the hemiwicking zipping dynamics (see Supplemental video). The corresponding zipping ratio has been derived from previous works [64-65], where the zipping ratio is also derived via an energy and mass balance on a hemiwicking configuration and is tied to a critical contact angle [65] that scales as \( \cos \theta_c = -1 + 2h/(2h + s_k) \). Also, while we
demonstrated that photoisomerization of SP induces systematic modulations in the surface energy, aside from changes in the static contact angle, the cameras used in this study were unable to detect the photoinduced changes in the meniscus curvature (κ). Refined studies are needed to understand the role of the photoinduced changes in κ and ∇κ. Also, while we demonstrated that photoisomerization of SP induces systematic modulations in the surface energy, aside from changes in the static contact angle, the cameras used in this study were unable to detect the photoinduced changes in the meniscus curvature (κ). Further experiments are needed to investigate the role of the photoactivated changes in κ and ∇κ.

The present work did not observe the pursued transition from static Cassie-Baxter (or Wenzel) state to the dynamic hemiwicking state based on the photoisomerization of SP on Au microstructured surfaces. Even with the use of different microstructures, the achieved photoisomerization of SP (i.e., ∆θ\textsubscript{CA}\textsuperscript{UV\leftrightarrowvis} ≈ 5-10°) is not sufficient to alternate between wetting states. Moreover, these surface free energy variations do not appear to be enough to overcome the solid-fluid absorption/binding energy for wetting state alternations at timescales appropriate for most fluid dynamic processes (i.e., timescales on the order tens of milliseconds or less). To achieve such multi-purpose surface switching (i.e., a surface that can self-wet and self-dry based on state of SP), surface free energy changes corresponding to ∆θ\textsubscript{CA}\textsuperscript{UV\leftrightarrowvis} > 30-50° are needed. The following expression has been utilized to scale the differential surface free energy (dG) per unit length (dx) for microstructured surfaces, namely with hemiwicking [75].
\[ dG = (\gamma_{SL} - \gamma_{SV})f_r(1 - \Phi)dx - \gamma\Phi dx + \gamma f_r \cos \theta dx \] (13)

Where \( f_r \) is the surface roughness factor and \((1 - \Phi)\) is the structure fraction remaining dry. Based on what has been discussed in this study regarding the achievable changes in \( \theta_{CA} \) (or the surface free energy), it can be concluded from Eq. (12) that the overall free energy per unit length will increase with photoisomerization of the SP coating. However, despite the expected increase in the overall surface free energy per unit length (based on the photoisomerization of SP), dramatic improvements in \( \Delta\gamma \) (or \( \Delta\theta_{CA} \)) are needed for new technologies based on the static-to-dynamic wetting state transitions discussed herein. Based on Eq. (12), such static-to-dynamic transitions will require changes in surface free energy that are much greater than the 13% achieved in this work.

Regarding hemiwicking future applications, while the demonstrated hemiwicking enhancements were only nominal, it still seems favorable to incorporate SP (or other photoactive compounds) in heat transfer systems such as heat pipes for actively tuning the overall heat transfer coefficient. This aspect of the design would take advantage of the additional chemically capillary action to increase or decrease the overall two-phase thermal transport. Moreover, applications based on photoactive imbibition, elastocapillary effects, and packed bed capillary tubes (wicks) seem promising based on the significant increase in solid-liquid surface area that be achieved with such systems. In principle, the performance limits of such devices can be rapidly accessed by simply measuring the photoisomerization-induced changes in the elastocapillary length or capillary gravity length.
2.5 Conclusion

As demonstrated in this study, the use of photoactive compounds on a microstructured Au surface affects the surface wetting between the two different states. In both smooth and microstructured Au, changes in the wetting dynamics were captured upon photoisomerization of SP through the static, dynamic, and apparent contact angle $\theta_{CA}$. Along with $\theta_{CA}$, changes in the diffusion of a polar fluid wicking through a microstructured array based on the orientation of SP were also recorded. Based on the observed changes in the $\theta_{CA}$ and diffusion, the different surface energies between the two different photoisomerization states were calculated through both the Owens-Wendt and Van-Oss models. Results presented in this work give the community a better understanding of the limitations of photoreactive surface coatings for the use in a variety of applications, including self-cleaning surfaces and thermal control devices. The slight variation of wetting behavior on the photoswitchable surface presents the possibility of having microstructured gold with controllable wettability. Further optimization is needed to maximize the photoisomerization-induced changes in the surface free energy (or, in terms of photoswitching the contact angle, $\Delta \theta_{CA}^{UV \leftrightarrow \text{vis}} > 30^\circ$). Such an optimization, combined with engineering the surface microstructure, will facilitate the design of photoactive fluid switches and thermal control systems.

2.6 Acknowledgements

The authors acknowledge the National Science Foundation. This material is based on research sponsored by the National Science Foundation (Grant No. 1653396). The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of the U.S.
Government (or departments thereof). Nanolithography fabrication of microstructures, as well as thin film deposition, took place at ORNL Center for Nanophase Material Sciences under User Proposal 2018-329, which is a DOE Office of Science User Facility.
2.7 References


CHAPTER 3 SUPPLEMENTARY INFORMATION OF CHAPTER 2

3.1 Materials and Instrumentation

Dichloromethane (CH$_2$Cl$_2$), acetonitrile (ACN), ethanol, and dichloromethane (DCM) were purchased from Fisher, USA. 2,3,3-trimethyl-3H-indole, 3-bromo-propionic acid, Diethyl Ether (Et$_2$O), ammonium acetate, salicylaldehyde, piperidine, 2-butanone, ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), cystamine dihydrochloride, and sodium chloride (NaCl) were purchased from Sigma-Aldrich, USA. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories, Inc., USA.

$^1$H spectroscopy was carried out with an NMR spectrometer (Avance III 400) from Bruker, USA. Absorbance experiments were performed using a UV-Vis spectrophotometer (Cary 50 Bio UV/Visible) from Varian, Australia.

1-(2-carboxyethyl)-2,3,3-trimethyl-3H-indolium bromide (1): The novel synthetic method was proposed to prepare 1. The 30 mL microwave reaction flask, equipped with a stir bar, was charged with 2,3,3-trimethyl-3H-indole (1.0 g, 6.28 mmol) and 3-bromo-propionic acid.
(0.961 g, 6.28 mmol) and ACN (15 mL). After 20 mins of microwave irradiation (150 psi, 200W), ACN was removed under reduced pressure to obtain a dark purple residue. Then, the residue was washed three times with DCM to remove unreacted starting material and was added dropwise to Et₂O which was surrounded by an ice bath to give a precipitate. A purple solid (final product with a yield of 72.9%) was obtained by filtration of precipitated residue. 1H NMR (400 MHz, DMSO-d6): δ 1.53 (s, 6H), 2.87 (s, 3H), 2.99 (t, J = 7.2 Hz, 2H), 4.66 (t, J = 7.2 Hz, 2H), 7.60-7.65 (m, 2H), 7.83-7.86 (m, 1H), 7.99-8.02 (m, 1H).

3,3-bimethyl-6-spiro-[2H]-1-benzopyran-2, 2-indoline: SPCOOH (2): The synthesis of 2 was modified following a literature procedure [1]. Briefly, 1-(2-carboxyethyl)-2,3,3-trimethyl-3H-indolium bromide (2.00 g, 5.57 mmol), salicylaldehyde 2a (0.59 mL, 5.65 mmol), and piperidine (0.56 mL, 5.66 mmol) in 2-butanone (16.7 mL) was refluxed for 3 h. The reaction products were extracted with CH₂Cl₂ and then the desired product was isolated by silica gel column chromatography with a step gradient from ethyl acetate/hexane in 3: 1 (v/v) to methanol/ethyl acetate in 1: 1 (v/v). After drying under reduced pressure, the purified product 3a was obtained as a reddish-brown powder in a yield of 74% (1.37 g, 4.10 mmol). 1H NMR (600 MHz, CDCl₃): Aromatic protons, 7.16(m,194, 2H), 7.07(J=5.1,0.6Hz,1.04,1H), 7.05(d,J=4.5Hz,1.05,1H), 7.01(dd,  J=8.5,4.2Hz,1.98, 2H), olifinic protons, 6.75(d,J=5.7 Hz,1.05,1H), 5.87(d, J=6.9Hz,1.00,1H), N1–CH₂–, 3.52(m,2.21,2H), CO–CH₂–, 2.67(m,2.19,2H), –CH₃(*2),1.27(s,3.38, 3H ),1.12 (s,3.01,3H).
3.2 H NMR spectra for compounds 1 and 2 (SPCOOH)

Figure 15 ¹H NMR spectra of 1-(2-carboxyethyl)-2,3,3-trimethyl-3H-indolium bromide
Figure 16 $^1$H NMR spectra of 3,3-bimethyl-6-spiro-[(2H)-1-benzopyran-2, 2-indoline]: SPCOOH
3.3 Optimizing the wavelength and irradiation time for ring opening and closing of SPCOOH

Figure 17 Absorption of the SPCOOH in the ethanolic mixtures. (a)-(d): Three cycles of the 254 nm of UV and 470 nm visible light followed by 365 nm UV and 520 nm visible light irradiation for 1, 2 and 3 minutes, respectively.

Irradiation of SPCOOH with 365nm UV and 520 nm Visible light shows a broader adsorption range (more photoisomerization. In addition, one minute of UV irradiation is enough to open the SPCOOH ring which is preferred as a shorter UV irradiation time results in less photo fatigue.)
Also, an increase of time for Visible light irradiation improves the reversibility of Merocyanine (MC) to SPCOOH.

It is worth mentioning that SPCOOH has different photoisomerization kinetics in ethanolic mixtures and the photoswitchable surface. This isomerization is prolonged in the Au surface due to the inflexible movement of SPCOOH in comparison to the solution (which results in a higher degree of freedom). In fact, the UV absorbance experiments in the ethanolic solution are the preliminary results required for the photoisomerization time on photoswitchable Au surface. These results were complemented by the contact angle results. Based on these two results, ten minutes of visible light irradiation show more reversibility of MC to SPCOOH in the Au surface.
3.4 Effect of components on the Photoswitchable contact angle

Figure 18 (a) The change in the contact angles after the different light exposures for the different steps in the photoswitchable surface (SPCOOH functionalized flat-Au and microstructured-Au [sample 3, Table 1 (manuscript)]). (b) UV-activated and (c) vis-activated apparent contact angle images for a 50:50 EtOH/water mixture on a microstructured, SPCOOH-functionalized pillar array [sample 2, Table 1 (chapter2)].

As shown in the Fig.18, photoswitching contact angle is observed in the presence of SPCOOH for both bare (flat) and microstructured Au. This shows the effect of reversible photoisomerization of SP on the hydrophilicity and hydrophobicity of Au surface. It is worth mentioning that un-uniform photoswitching behavior in the different steps of photoswitchable surface (SAM only, EDC, bare gold) represent the measurement errors as well as the intrinsic and extrinsic defects on polycrystalline surfaces.
3.5 Contact angle measurements for the photoswitchable surface

As shown in Table 4, applying SAM decreases the contact angle on both flat and microstructured Au which is due to the hydrophilic terminal amino group of the SAM. On the other side, the contact angle of the photoswitchable surface (in the presence of SP (SP/SAM)) behaves differently for the flat and microstructured Au.

Table 4 The Contact Angles for Initial SAM and SPCOOH

<table>
<thead>
<tr>
<th>Surface Type</th>
<th>Initial</th>
<th>SAM</th>
<th>SP/SAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat(smooth) Au</td>
<td>83.99 ± 2.91</td>
<td>71.01 ± 2.63</td>
<td>69.25 ± 4.96</td>
</tr>
<tr>
<td>Microstructured Au</td>
<td>122.00 ± 4.36</td>
<td>92.54 ± 13.69</td>
<td>108.97 ± 5.51</td>
</tr>
</tbody>
</table>

The hydrophobicity of SP is expected to increase the contact angle of the photoswitchable surface (SP/SAM). Nevertheless, this is only observed in the microstructured Au. For the flat Au, SP/SAM’s contact angle (69.25 ± 4.96) is close to that of SAM (71.01 ± 2.63). This small change can be due to the uneven distribution of SP on the Au surface caused by intrinsic and extrinsic defects on the polycrystalline surfaces (J.C. Love, L.A. Estroff, J.K. Kriebel, R.G. Nuzzo, G.M. Whitesides, Self-assembled monolayers of thiolates on metals as a form of nanotechnology, Chem. rev., 105(4) (2005) 1103-1170). These defects can cause the formation of non-uniform SAMs and SP/SAM which result in a negligible variation in their contact angle.
3.6 Optimizing the concentration of SPCOOH

![Graph showing contact angle changes](image)

**Figure 19** Contact angle changes in the SP functionalized Au substrate (two concentration of SPCOOH in the ethanolic solution was used)

A higher concentration of SPCICOOH (7.5 mM) was used to increase the photoswitching of the Au surface. However, as demonstrated in Figure S6, it has a detrimental impact on photoswitching, and in fact reduces it. This can be due to the uneven distribution of SP on the Au surface caused by the intrinsic and extrinsic defects found in the SAMs formed on polycrystalline surfaces. (J.C. Love, L.A. Estroff, J.K. Kriebel, R.G. Nuzzo, G.M. Whitesides, Self-assembled monolayers of thiolates on metals as a form of nanotechnology, Chem. rev., 105(4) (2005) 1103-1170; [https://doi.org/10.1021/cr0300789](https://doi.org/10.1021/cr0300789)).
3.7 Deviations in the applied model for surface tension from the effective medium theory (EMT)

![Graph showing surface tension as a function of water molar fraction.](image)

*Figure 20 An estimation of the surface tension of the water-ethanol mixture based on the molar fraction and the effective medium theory (EMT)*

An understanding of the surface tension of the water-ethanol mixture is provided since the total surface tension is needed to solve the Oss-Wendt and the Oss Good models for surface wetting. Two methods are presented to estimate the surface wetting. The first method is an estimation based on the molar fraction of the two fluids. The following equation is used to estimate the surface tension [2].

\[
\sigma_{\text{hybrid}} = \gamma_1^L - \left(1 + \frac{bx_1}{1 - ax_1}\right)(x_2)(\gamma_1^L - \gamma_2^L)
\]  

(1)
Where define the variable based on the studies in [3]. Meanwhile, the effective medium theory (EMT) looks at the total surface tension as the average sum of the components to the water-ethanol mixture, which is summarized through the following equation. For this study, the MET approach was taken.

\[
\sigma_{hybrid} = \sum_{i}^{N} v_i Y_i
\]  

\[ (2) \]

3.8 Contribution of polar/nonpolar components on contact angle variations

![Graph showing the expected ratio of the polar to nonpolar component of surface tension as a function of the change in the contact angle of SP functionalized Au surface based on the Oss-Wendt model.](image)

Figure 21 The expected ratio of the polar to nonpolar component of surface tension as a function of the change in the contact angle of SP functionalized Au surface based on the Oss-Wendt model.

These results show that changing the contact angle increases the effect of polar to non-polar component of SP. Positive and negative charges exposed in the ‘open’ SP state are
representative of the nitrogen and oxygen molecules, respectively (see Fig. 2(b)). Based on the Van Oss models, it is observed that the main changes in the polar component of the surface energy are caused by the electron donating (i.e., base) component. This indicates that the negative charges on oxygen molecules in the ‘open’ SP state are more influential in altering the overall surface tension than the positive charges on nitrogen molecules.
3.9 Variation of contact angle as a function of volume percentage

These results show that when the volume of ethanol increases, the contact angle decreases. This is due to ethanol’s lower polarity and intermolecular forces when compared to water which leads to a decrease in the contact angle of the Au surface.

Figure 22 Variation of contact angle as a function of the volume percentage of ethanol in the water/ethanol mixtures used for both the surface free energy scaling and the hemiwickng experiments.
3.10 Hemiwicking model and UV-vis wicking results

Figure 23 Schematic of the hemiwicking model parameters for both Sluggish Climb (SC, top) and Rapid Ascent (RA, bottom) based on a meniscus curvature tied to the contemporary meniscus curvature $\kappa$ used in capillary rise flow in capillary tubes.

For this work we derive the wicking/pumping force per unit cell width based on the contemporary capillary rise problem with a meniscus curvature scaling as $\kappa \sim 2 \cos(\theta_{CA}^* + \beta)/s_\kappa$, where $\beta$ is the slant angle of the pillar walls relative to the substrate surface normal, $s_\kappa$ is the interpillar gap separation, and the Laplace pressure scales as $\Delta P = \sigma\kappa$. In result, a force balance between the viscous drag and wicking force ($f_w \approx f_{C_{do}}$) leads to the generalized solution for the solid-liquid Surface texture,
\[ K = \frac{2 \cos(\theta_{CA}^* + \beta)}{s_x} \left[ \frac{A_w}{A_{C,do}} \right] L_C \left( \frac{s_x}{\cos \alpha} - d^* \right), \]  

(3)

Where \( \theta_{CA}^* \) is the equilibrium contact angle of the fluid meniscus in contact with the pillar wall, \( \frac{A_w}{A_{C,do}} \) is the ratio of the pillar surface area for pumping/wicking to drag per unit cell, \( L_C \) is the characteristic length for the flow-field (\( \text{Re} = \rho U_L C / \mu \)), and the \( (s_x/\cos \alpha - d^*) \) term accounts for packed bed limit with \( d^* = d \) for cylindrical pillars. Thus, the wicking model accounts for light-activated changes in the wetting behavior \( \theta_{CA}^{UV \leftrightarrow vis} \) and anisotropic pillar geometries \( \beta \neq 0 \), where \( \beta = 0 \) for symmetric pillars (e.g., cylinders, squares, or rectangles) and \( \theta_{CA}^* \) corresponds to the effective contact angle with the flat wall (or that relative to the surface normal of pillar wall), not the apparent contact angle of the fluid with the microstructured surface.

Figure 24 Hemiwicking images for (left) open form (UV irradiation) and (right) closed form (Visible irradiation) of the SP-functionalized, Au-coated pillar array. The wicking array is of short, cylindrical pillars \( (h=10 \text{ um}) \), where the fluid \( (75:25, \text{EtOH/water}) \) does not wick up the entire array. Thus, the images correspond to the maximum wicking distance.
Figure 25 Snapshot hemiwicking images for (left) open form (UV irradiation) and (right) closed form (Visible irradiation) after 0.5 seconds of hemiwicking with the SP-functionalized, Au-coated, anisotropic pillar array [sample K, Table 1 (manuscript)] with a 75:25 (EtOH/water) fluid mixture.

Hemiwicking results show the change from closed to open formed SP is not sufficient to alternate between Wenzel and hemiwicking states. The findings indicate that although there is a change in the surface free energy (via photoisomerization of the SP surface coating), it is not sufficient to overcome the solid-fluid absorption/binding energy to alternate between the Wenzel and hemiwicking states. Moreover, the UV light activation was not enough to increase the effective surface free energy to cause extended hemiwicking and to overcome the capillary gravity length.
3.11 References


CHAPTER 4 PHOTO-SWITCHABLE CONDUCTIVITY OF POLYANILINE USING VISIBLE-LIGHT ACTIVATED METASTABLE-STATE PHOTOACID

4.1 Abstract

Herein, we present an innovative photoswitchable and flexible film which allows for shifting between the conductivity patterns of PANI. The film is composed of a visible light sensitive mixture drop casted on the Polyethylene terephthalate (PET) substrate precoated with a conductive PANI-ES layer. The electrical conductivity of the film is modulated by visible light induced proton transfer from the metastable state photoacid (mPAH). Upon 10 minutes irradiation of the film, mPAH releases protons that are captured by the PANI-EB in the light sensitive layer and increases the film’s conductivity by 2.6 times (0.0025 to 0.0065 S/cm). However, in the dark, mPAH recaptures the protons and decreases the film’s conductivity. Additionally, in the absence of PANI-EB in the drop casted layer, reverse conductivity behavior is observed. Herein, the film’s conductivity decreases after irradiation of light and increases in the dark. This reverse behavior might be explained by photoinduced proton transfer in the interface of the light sensitive layer and the PANI-ES precoated PET. Multiple characterization techniques such as Ultraviolet Visible Spectroscopy (UV-Vis) were used to investigate the expected and reverse photoswitching behaviors. The findings of this study can help design potential devices that can both increase and decrease conductivity in response to light irradiation. This advancement may have applications in the information processing and recording area.
4.2 Introduction

Polyaniline (PANI) is one of the most promising conducting polymers, with applications spanning from semiconductors and supercapacitors to energy storage, biosensors, coatings, and organic electronic materials [1-7]. It has been of great interest to scientists due to the ease of synthesis, low cost, and tunable properties such as electrical conductivity and high environmental stability [8-11]. Conductive PANI can be polymerized and deposited as an adherent layer on a variety of substrates including natural fibers, glass, silver chloride pellets, textiles, and plastic, which expands its application range [12-17]. Depending on the protonation degree (Fig. 26), PANI can change from a conductive salt (PANI-ES) to a nonconductive base (PANI-EB) (10⁻⁹ S/cm) [18]. PANI's conductivity has been modulated by harsh acidic and basic conditions that are difficult to control and manipulate [24]. As a result, new ways for controlling PANI's conductivity are needed for microelectronics development.

Light is a great alternative to harsh acidic and basic conditions because it is a non-destructive, clean energy source that can be easily manipulated [19]. Organic light sensitive compounds such as Photoacid Generator (PAG) and Spiropyran (SP) have been used to modulate conductivity in PANI film [20-27]. Upon irradiation with light, PANI converts to strong acid which is used to modulate the conductivity of PANI. Liao et al. [24,25] improved the conductivity of PAG/PANI composite films to 10⁻¹ S/cm by implementing proton transfer polymers and improving the molar ratio of thin films.
Nevertheless, PAG is irreversible due to its instability and high decomposition rate when irradiated. Guo et al [26] and Kim et al [27] modulated the conductivity of PANI through the reversible uptake and release of protons using SP. The conductivity of SP/PANI film was significantly reduced after ten minutes of UV irradiation [26]; but was only recovered after eight hours of visible light irradiation. Another adverse effect of this method was that the UV irradiation could pose difficulties in terms of bio applicability and photo fatigue. The PAG/PANI and SP/PANI composite films were deposited on quartz [20,21,26,27], silicon wafer [22,23] and on glass substrates [24,25]. The films formed on these substrates have a conductivity ranging from $10^{-7}$ S/cm to $10^{-1}$ S/cm [20-25] but are rigid and costly. The composite films contained mostly PANI-EB and were fabricated using spin casting [22-25], drop casting [21] and dip coating [26].
Figure 26 Basic structure of PANI and different redox forms of PANI with its doped states [1-2].
PANI's conductivity has been modulated by harsh acidic and basic conditions that are difficult to control and manipulate [24]. As a result, new ways for controlling PANI's conductivity are needed for microelectronics development.

In 2011, Liao introduced the Metastable-State Photoacid (mPAH) [28], mPAHs are composed of electron accepting (EA) and slightly acidic nucleophilic (NuH) moieties joined by a double bond (Fig. 5(a)). The irradiation of visible light induces a trans-cis isomerization of the double bond, allowing a nucleophilic cyclization reaction to take place between these two moieties and release a proton. Upon irradiation with visible light, the mPAH changes from a weak to a strong acid. Contrary, in the dark, the metastable form relaxes to the original form and uptakes the proton (Fig. 5 (b)). In 2012, Shi et al [29] proposed to reversibly modulate the conductivity of
PANI using a composite of PANI-EB and mPAH. To make a uniform composite film, PEG and Poly (acrylic acid) (PAA) was mixture. Thin films were prepared by spin casting on glass substrates. However, the magnitude of photoswitchable conductivity increased only by two times of initial conductivity, because mPAH released most of its proton to the PANI-EB before irradiation of the film [30]. Alternatively, PEG, PAA and PANI-EB might form hydrogen bonds over time, doping the PANI-EB’s conductive sites (quinoid diamine repeat units).

Herein, we propose a new photoswitchable conductive film which consists of an mPAH visible light-sensitive mixture (contain of PVC, plasticizer, and cyclohexanone) drop casted on a flexible PET substrate precoated with a PANI-ES layer. The precoating of PET with PANI-ES layer converts it to a conductive flexible substrate. Thus, the conductivity of the film can be modulated upon irradiation with visible light, in a simple and inexpensive way. The proposed photo-modulating mechanism for conductivity film is presented is Fig. 27.

![Figure 27 Proposed photo-modulating mechanism](image-url)
4.3 Experimental

4.3.1 Materials and characterization

Hydrochloric acid (12.1 molar), 1-(2-Nitrophenoxy) octane (NPOE), PANI-EB (MW = 20,000) and high molecular weight poly (vinyl chloride) (PVC) were purchased from Sigma-Aldrich, USA. Cyclohexanone 99.8% was purchased from Acros Organics (Fair Lawn, NJ). Heat-Stabilized Clear PET thin film (0.127-millimeter thickness) was purchased from Melinex ST505, USA. mPAH was synthesized according to the literature procedures with some modifications (Fig. 28 [31]).

![Synthesis route of modified mPAH](image)

*Figure 28 Synthesis route of modified mPAH: ((E)-3-(2-(2-Hydroxy-4-(octadecyloxy)styryl)-3,3-dimethyl-3H-indol-1-ium-1-yl)propane-1-sulfonate [31].

For the photo-switchable conductivity experiments, visible light activation was used. A 120 LED array (maximum average power of 1800 mW) from Elixa, USA was used to generate visible light at 470 nm. Conductivity experiments were measured using a source-meter unit (Keithley Source-Meter model 2400, Cleveland, OH). Film thicknesses was measured using a profilometer - Stylus (Bruker Dektak XT). A UV-Vis spectrophotometer (Cary 50 Bio UV/Visible)
from Varian, Australia was used for absorption measurements. The Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDX) analysis was conducted with a Zeiss ULTRA-55 FEG SEM. The X-ray photoelectron spectroscopy (XPS) experiments were conducted using a Physical Electronics 5400 Electron and Spectroscopy for Chemical Analysis (ESCA).

4.3.2 Fabrication and photoirradiation of the film

The photoswitchable conductive film is composed of a mPAH light sensitive film drop casted on top of the flexible PET substrate precoated with a PANI-ES layer. The manufacturing process of the photoswitchable conductive film is presented in Fig. 29.

![Figure 29 The preparation process of the photo-switchable conductive film.](image)

PANI is synthesized by in-situ polymerization of Aniline (AN) on top of the PET sheet. First, 0.43 g of ammonium persulfate (APS) oxidizing agent [31-35] is added to a beaker
containing 20 ml of 1 M Hydrochloric Acid. Then, 0.14 g AN is added and the mixture is stirred. Immediately after, the PET substrate (with dimensions of 2.54 * 8.89 cm) is placed in the beaker for 6 and 10 minutes. The PET is then rinsed with deionized (DI) water to remove unreacted compounds followed by gently drying it with nitrogen gas. The studied molar ratios of HCl/AN were tested to 1:1 and 2:1 with HCl set at 0.1, 0.2, 0.4, 0.8, 1 and 2 to get the lowest acid concentration necessary to form a conductive PANI-ES layer. In addition, XPS analysis was used to monitor the completion of polymerization [36-41]. Meanwhile drying the PET substrate precoated with PANI-ES, a mPAH light sensitive mixture was prepared. The mixture is composed of mPAH to induce proton release upon irradiation with visible light, PVC to make a uniform film after solvent removal, NPOE plasticizer to facilitate proton transfer and PANI-EB to induce conductive sites (quinoid diamine repeat units). These repeat units can get protonate and make the PANI-EB to PANI-ES. The addition of PANI-EB to the light-sensitive film increases PANI's ability to receive protons from the irradiated photoacid. The mixture of 66mg PVC, 33 mg NPOE, 2.5 mg PANI-EB and 1.5 mg of mPAH (45.0 mmol/kg) is dissolved in 700 μL of cyclohexanone. The mixture is then vortexed for 15 minutes to obtain a homogeneous cocktail solution. The PET substrate precoated with PANI-ES layer is cut in 2.54 * 8.89 cm. Subsequently, 50 μL of light sensitive cocktail is drop casted onto the obtained PET slices. The resulted photoswitchable conductive film is placed in a vacuum at room temperature for 48 h to remove the solvent. Afterwards, the PET slices are stored in desiccators for conductivity measurements. The thickness of the films was measure 30μm by profilometer. Two other films are fabricated in the same HCl/AN ratios without mPAH or PANI-EB. These films were used as a control experiments.
Conductivity experiments are performed in the dark over 3 cycles of photo-switching. A cycle of photo-switching consisted of 470 nm visible light irradiation for 10 minutes followed by leaving the film in the dark for 20 minutes (the maximum absorption peak of mPAH occurs at 470 nanometers. According to the UC-VIS spectroscopy results of the photoswitchable film, a time of between 10 and 20 minutes is sufficient for proton release and uptake, respectively).

The conductivity before and after irradiation was measured by I–V (current-voltage) scan using the two probe conductivity measurements as shown in Fig. 30.

*Figure 30 Performing the conductivity experiment by two probe methods*

Based on Ohm’s law: \( I = \frac{1}{R} V \), the slope of the current vs voltage plot gives \( \frac{1}{R} \) in which \( R \) is the resistance. Then conductivity can be calculated using: \( C = \frac{l}{RWH} \) (\( l \), \( W \) and \( h \) are length, width, and thickness of the photoswitchable conductive film).
4.4 Results and discussion

4.4.1 Photo-switchable conductivity

The minimum acid concentration required to form a conductive PANI-ES coating layer based was 0.4M. A higher concentration of HCl resulted in a greater number of protons. This increased the conductivity of the PET substrate to the point where variations in the film conductivity induced by the light sensitive layer became negligible.

Independent to the presence or absence of PANI-EB, the film without the mPAH does not display photoswitchable conductivity (Fig. 31 (a) blank 1-3). Also, conductivity results show that the presence of PANI-EB in the light sensitive film change the conductivity behavior. In the presence of PANI-EB, photoswitching takes place in the quinoid diamine repeat units as illustrated in the proposed mechanism (Fig. 27). Upon visible light irradiation, mPAH releases protons which are captured by the PANI-EB, converting it to PANI-ES (enhancing conductivity). Furthermore, in the dark mPAH recaptures the protons from the PANI-ES and switches it to PANI-EB (decreasing conductivity). The conductivity of the photoswitchable film increases from 2.6 times (Light 1/Dark 1) in the first cycle to 1.6 times (Light 3/Dark 3) in the third cycle (Fig. 31 (a)). (This decrease in conductivity during these three cycles may be due to the photodegradation of mPAH in the photoswitchable film). The findings are consistent with the proposed mechanism (Fig. 27). On the other hand, in the absence of PANI-EB, photoswitching is reversed, with conductivity decreasing upon photoirradiation and increasing in the dark. Although 2.6 times increase in conductivity is less than a ten-fold increase using PGA) [24-25], it is reversible (by using mPAH). The main limitation of this research is that it was not reproducible.
Also, the results show that the conductivity of the photoswitchable film decreases from 1.9 times (Dark 1/Light 1) in the first cycle to 0.8 times (Dark 3/Light 3) in the third cycle (Fig. 31 (b)). In both films containing PANI-EB and films without PANI-EB, there is a decreasing conductivity change ($\frac{\Delta C}{C} \times 100$) over three cycles which might be attributed to the mPAH photodegradation.

![Conductivity results over 3 cycles of photo-switching](image)

**Figure 31** Conductivity results over 3 cycles of photo-switching (a) films containing PANI-EB ($\frac{\Delta C}{C} \times 100$): cycle 1 = 1.6 to cycle 3 = 0.66 (b) films without PANI-EB ($\frac{\Delta C}{C} \times 100$): cycle 1: 0.80 to cycle 3: 0.32 (Blank samples don’t have mPAH. Three samples were used to study reproducibility of results)

Based on the conductivity results, there are two possible mechanisms for light induced proton transfer in the photoswitchable film. These mechanisms are dependent on the presence or absence of PANI-EB in the drop casted light sensitive film (Fig. 32). The proposed mechanism occurs in the presence of the PANI-EB in the light sensitive film. Herein, upon irradiation of 470
nm visible light on the photoswitchable film, PAH releases its protons which can be captured by PANI-EB increasing its conductivity (Fig. 32 (a)). This proton transfer depends on a) the acidity constant (pKₐ) of excited state mPAH and b) the rate of the proton transfer within the light sensitive polymeric film.

The second mechanism, describing the reverse behavior, takes place in the absence of PANI-EB in the light sensitive film. As a result, the conductivity of the photoswitchable film is only determined by PANI-ES. In this case, upon irradiation with visible light, PAH releases protons in the light sensitive film. These protons can spread throughout the film and aggregate in

\[ \text{Figure 32 Possible mechanisms for photoinduced proton transfer of mPAH in the photoswitchable film in: a) the presence of PANI-EB. b) the absence of PANI-EB} \]

the interface between the light sensitive film and the PANI-ES layer. Aggregated protons can potentially act as a blocking agent and prevent the flow of electrons in the PANI-ES layer which decreases the electrical conductivity of the photoswitchable film. Contrary, in the dark, PAH uptakes its protons and increase the conductivity of PANI.
4.4.2 Characterization techniques

4.4.2.1 UV-VIS spectroscopy

UV spectroscopy was used to monitor the photoswitchable conductivity of the films in the presence (proposed mechanism) and absence of PANI-EB (reverse mechanism) as shown in Fig. 33. Visible light irradiation of the light sensitive photoisomerizes the PAH, causing a decrease in the absorption peak intensity around 470 nm. This represent the conversion of mPAH to the conjugated form (metastable Spiropyran) or photoinduced proton release process which is independent of the presence and absence of PANI. The PANI-ES conductive layer is characterized by a peak at 850 nm in photoswitchable films. A noticeable difference between these two films is the absorption intensity around 470 nm region, which representing PAH. The intensity of the 470 nm peak is ~1.9 in the films with PANI-EB (Fig. 33(a)) and ~3.6 in the films without PANI-EB (Fig. 33(b)).
Figure 33 Absorption of a photoswitchable film in a) presence of PANI-EB and b) absence of PANI-EB.

The absorbance results do not support the conductivity behavior in the films. As previously stated, upon light irradiation of the film containing the PANI-EB (Fig. 33(a)), mPAH releases protons which can be captured by PANI-EB, converting it to PANI-ES. Thus, an increase in the absorption intensity of PANI-EB around 600 nm and decrease around 850 nm is expected (Fig. 34(a)). Nevertheless, these peak shifts are not observed in the absorbance results of the photoswitchable films. These may be due to a lack of photoinduced proton transfer to the PANI-EB, as mentioned, due to a) the acidity constant of the excited state mPAH ($p_{ka^*}$) b) the low rate of proton transfer inside the light sensitive polymeric film. Based on the UV results and the Henderson–Hasselbalch equation and extracted results(Fig. 34), the acidity constant ($p_{ka^*}$) of PANI is around 4.
To capture photoinduced proton by PANI-EB, acidity constant of the excited state mPAH \( (pK_a^*) \) should be less than 4. In reality, there is no exact method for determining \( pK_a^* \). Foster Cycle dose give a good approximation to predict \( pK_a^* \) which is based on the ground state \( pK_a \) and energy difference between deprotonated and protonated mPAH:

\[
pK_a^* = pK_a + \frac{(E_{PAH} - E_{mPAH})}{2.3RT}
\]

Where, \( R \) is gas constant and \( T \) is 298K. Based on the absorption results, it seems that \( Pk_a^* \) might be close to 4 (\( Pk_a \) of PANI-EB); so, can be the reason of low photoinduced proton transfer.

Regard to the film without PANI-EB, upon photoisomerization of mPAH, there is no change in the PANI absorbance results. This shows that absorption results can’t support the reverse photoswitching conductivity behavior.
### 4.4.2.2 SEM-EDX results of the polymerized PANI-ES layer and visible light sensitive film

SEM-EDX was utilized to examine the reverse photoswitchable conductivity and morphology of the light sensitive film. The surface chemistry of the PANI-ES layer was examined using XPS.

Fig. 35 and 36 show the vertical and cross section SEM images of the PANI-ES layer. Generally, the polymerization of PANI takes place in three steps: 1) growing the oligomeric radical cation (primary nucleation or initiation in first three minutes of reaction) 2) adhering the polymer chain on the surface after 3-8 minutes (secondary nucleation or propagation) and 3) completing the polymerization after 8-12 minutes (termination) [32-36]. Fig. 35 shows that 10 minutes of polymerization (d, e and f) results in a denser granular morphology compared to 6 minutes of polymerization (a, b and c). This indicates that polymerization is not completed after 6 minutes (secondary nucleation step). Furthermore, the cross-section SEM pictures (Fig. 36) show that 10 minutes of polymerization produces a more homogeneous and packed polymer morphology (d, e, f) than 6 minutes of polymerization (a, b and c). As the polymerization progresses, this packed architecture produces a higher molecular weight PANI. These results indicate that 10 minutes of polymerization (Fig. 36) may produce a consistent PANI-ES layer for a photoswitchable conductive film. Despite this, a denser granular structure in the PANI-ES may act as a blocking agent and prevent the flow of electrons in the PANI-ES layer which decreases the electrical conductivity of the photoswitchable film.

Fig. 37 shows both the vertical and cross section SEM images of the light sensitive film on top of PANI-ES layer. Both vertical (a, b, c) and cross (d, e, f) section SEM results show formation
of a uniform film with considerable amount of entrapped gas bubble (spherical morphologies) [42-46]. These bubbles decrease the quality of light sensitive film, resulting in a smaller change in conductivity in the photoswitching experiments.

4.4.2.3 EDX results of polymerized PANI-ES layer and visible light sensitive film:

Fig. 38 shows the EDX analysis of the components in the photoswitchable film. These results are supporting the SEM analysis (higher weight percent of carbon and nitrogen over 10 minutes (Fig. 38 (a)) represents the higher molecular weight of PANI-ES and completion of the polymerization). Also, increasing polymerization time will enhance the oxidation percentage of the PANI-ES layer.

Figure 35 Vertical-section SEM images of in situ polymerized PANI on the surface after 6 minutes (a, b, c) and 10 minutes (d, e, f) with different magnifications (a, d): 1 KX, (b, e): 5 KX, (c, f): 10 KX
Figure 36 Cross-section SEM images of in situ polymerized PANI on the surface after 6 minutes (a, b, c) and 10 minutes (d, e, f) with different magnifications (a, d): 10 KX, (b, e): 25 KX, (c, f): 50 KX

Figure 37 Vertical (a, b, c) and cross (d, e, f) section SEM images of the light sensitive film on top of PANI-ES layer with different magnifications (a, d): 1 KX, (b, e): 5 KX, (c, f): 10 KX
By comparing the EDX images of the PANI-ES layer (Fig. 38 (a), (b)) and the light sensitive film on top of it (Fig. 38 (c)), it is concluded that the higher percentage of C represents the formation of the light sensitive film (presence of PVC in the film). Furthermore, a higher oxygen percentage indicates film oxidation and the presence of entrapped air bubbles (as was shown in SEM results). Also, Fig. 38 (d) shows picture of light sensitive film on top of PANI-ES layer. As this picture shows, the light-sensitive film is not uniform, which is a problem of drop-cast films.

![EDX results of in situ polymerized PANI on the gold surface](image-a)

![EDX results of the light sensitive film on the top of deposited PANI](image-b)

![EDX results of the light sensitive film on the top of PANI-ES layer](image-c)

![Picture of light sensitive film on top of PANI-ES layer](image-d)

*Figure 38 EDX results of the in situ polymerized PANI on the gold surface (a) after 6 min, (b) 10 min, (c) light sensitive film on the top of deposited PANI, (d) picture of light sensitive film on top of PANI-ES layer*
4.4.2.4 Surface chemistry analysis

The spectrum and elemental composition of the in situ polymerized PANI (PANI-ES layer) was measured by XPS and compared with theoretical amounts (Fig. 39 and 40). Results show that polymerization of PANI is not completed (presence of oxygen and sulfur on the surface). The C1s spectrum (binding energy ranging ~ 282–286 eV) is a result of the formation of an aromatic ring in the PANI-ES. The presence of the C-C: 284.8 eV, C-H~ 286 eV confirm the polymerization and the presence of the C-S bond: ~284.5, C-N: ~285.5, C-Cl: ~ 285.2 and oxidation of the PANI-ES at the C-O-C: ~ 286 eV. Also, the N 1s region (binding energy ~ 397–400 eV) confirms the formation of nitrogen bonds in the PANI-ES (peaks at ~ 399.5 and ~ 400.8 eV can be attributed to the N-H and N-C, respectively). Another evidence of the oxidation of the PANI-ES layer is the O 1s spectra (binding energy 529-533 eV). The incomplete polymerization of PANI (presence of oxygen, sulfur, and chlorine in the surface) can decrease the quality of the PANI-ES layer. The mPAH photoinduced protons can entrap in low quality surface and prevent the flow of electrons in the PANI-ES layer which decreases the electrical conductivity of the photoswitchable film.
Figure 39 XPS analysis of the in situ polymerized PANI on the gold surface over 10 minutes. a) XPS survey b) Theoretical and Experimental percent composition (calculated as C$_{24}$H$_{20}$N$_{4}$Cl$_{2}$[47,48])

<table>
<thead>
<tr>
<th>Component</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>S</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Experimental</td>
<td>70.53</td>
<td>11.46</td>
<td>11.76</td>
<td>3.13</td>
<td>3.12</td>
</tr>
<tr>
<td>% Theoretical</td>
<td>80</td>
<td>13.3</td>
<td>N/A</td>
<td>N/A</td>
<td>6.7</td>
</tr>
</tbody>
</table>
Figure 40 XPS survey of polymerized PANI-ES layer on the PET substrate with changing the molar ratios of $\frac{[HCL]}{[AN]}$. 

(a) $\frac{[HCL]}{[AN]} = 1$ 

(b) $\frac{[HCL]}{[AN]} = 2$ 

(c) $\frac{[HCL]}{[AN]} = 3$ 

(d) $\frac{[HCL]}{[AN]} = 4$
4.5 Summary

This experiment describes the fabrication of a photo-switchable conductive film by photo inducing the proton transfer of mPAH. This allows for a controlled way of modulating the conductivity of PANI. Herein, we developed this technology on PET flexible thin film with increased conductivity. This advancement may have potential applications in the information processing and recording area. When mPAH is present in a film, the conductivity will increase when exposed to light and decrease in the dark. This photographswitchable conductive film can be used to communicate ensembles of two independent components capable of converting a visible light signal into an electrical signal via a reversible, photoswitchable proton transfer process. This application of photographswitchable conductive film allows for the input information to be written optically and read electrically.

The film was composed of a visible light-sensitive mixture drop-casted on the PET substrate precoated with a PANI-ES layer which simulates the acid doping-dedoping forms of PANI. Upon 10 minutes irradiation with 470 nm of visible light, mPAH released protons which are captured by the PANI-EB and converted to PANI-ES. This increased the conductivity of PANI by 2.6 times (0.0025 to 0.0065 S/cm). Contrary, in the dark, mPAH recaptured the protons from PANI-ES and switched it to PANI-EB. The presence of PANI-EB in the light sensitive film induces the expected photo-switchable conductivity behavior. On the other hand, the absence of PANI-EB causes the reverse conductivity behavior (increase of electrical conductivity in the dark and reduced conductivity the light). This reverse behavior can be explained by the fact that
photoinduced protonation of mPAH produces blocking agents in the PANI-ES, which prevent electron transport. The SEM-EDX showed the presence of considerable amount of gas bubble defects which decreased the quality of the light sensitive film that may reduce the change of the photoswitchable conductivity. These findings can serve as inspiration for future development of the photo-switchable conductive films. Further works are needed to obtain reproducible results using the photoswitchable conductive films, which may include fabrication of more uniform films or the use of mPAH compound with higher acidity coefficient of the excited state mPAH (pKₐ*).

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