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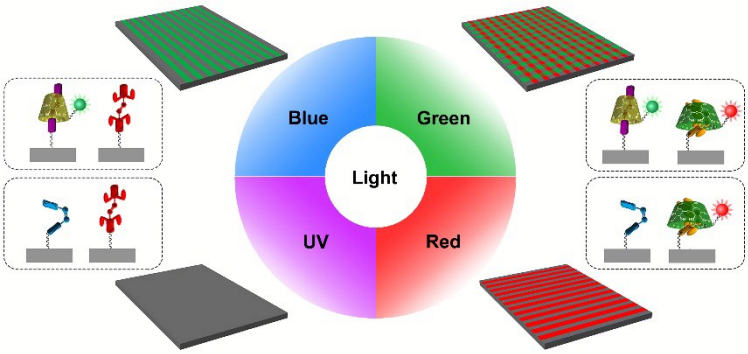
TOC

Four independent states are orthogonally photo-controlled and switched by ultraviolet, blue, green and red light irradiations on micropatterned surfaces.



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Orthogonal Photo-switching of Supramolecular Patterned Surfaces

Dongsheng Wang,[a] Frank Schellenberger, [b] Jonathan T. Pham,[c] Hans-Jürgen Butt,[b] and Si Wu*[b]

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We used Azo/α-CD and ipAzo/γ-CD host-guest complexes to demonstrate that four independent stable states can be orthogonally photo-switched by UV (365 nm), blue (470 nm), green (530 nm) and red light (625 nm). A supramolecular patterned surface was fabricated and orthogonally photo-switched by light with different wavelengths.

Orthogonal switching can be used to control multiple functions within a single material system by two or more independent external stimuli (*e.g.*, pH, heat, light and chemical) [1]. In contrast to traditional stimuli-responsive systems, which are switched between two states, orthogonal systems can be triggered into three or more states having a wider range of possible functions [1a, 2]. However, the reported orthogonal switchable systems are controlled by stimuli with different types (i.e., light/heat [1a, 1c], pH/chemical [1b] and heat/chemical [1d, 1e]), and the research on orthogonal switching systems by one-type of stimulus remains an unsolved challenge.

Light has been widely used to control processes and functions in chemistry and material science as an external stimulus because it can be applied with high spatial and time resolution [3]. Photoresponsive materials have been successfully applied in the fields of biomedicine, nanoscience, hydrogels, and surfaces [3b, 3d, 4]. Typically, chromophores responsive to light are integrated in the material systems, which can be switched between two independent states upon light exposure, and hence can display two different functions. However, these "switch"-type photoresponsive materials are limited to only two functional states ("on" and "off"), and are insufficient for functioning in an environment with a complex range of light stimuli. On the other hand, orthogonal photo-controllable systems possess a "mode dial"-type property that can switch between ≥3 states under control of ≥3 lights with different wavelengths. However, most photoresponsive chromophores have heavily overlapped absorption in the ultraviolet (UV)-visible region, which is one of the biggest challenges in the advancement of photoresponsive orthogonal systems [3e, 5].

Azobenzene (Azo) and cyclodextrin (CD) have been extensively investigated for designing photoresponsive supramolecular materials [6]. Under dark or visible light irradiation, *trans* Azo can enter the hydrophobic cavity of α-CD to form a strong 1:1 host-guest complex. Under UV light irradiation (~365 nm), *trans* Azo switches to *cis* form, and the host-guest complex dissociates due to hydrophilicity of the *cis* Azo and unfitted molecular scale with the α-CD cavity [6]. In our previous work, we synthesized tetra-ortho-isopropoxy-substituted Azo (ipAzo), which shows *trans*-to-*cis* isomerization under green or red light irradiation (530 or 625 nm), and *cis*-to-*trans* isomerization under heating, UV or blue light irradiation (365 or 470 nm). *cis* ipAzo forms a 1:1 host-guest complex with γ-CD, while the host-guest interaction between *trans* ipAzo and γ-CD is weak [7]. The result is the reverse of Azo/α-CD complex.

Here, we combined ipAzo/γ-CD with the Azo/α-CD host-guest complex to fabricate photo-switchable supramolecular micropatterned surfaces. 4 states can be orthogonally controlled by UV, blue, green and red light. Patterned surfaces are important for a number of fields related to materials and nano science [8]. In particular, photoresponsive patterned surfaces can be fabricated with switchable wettability, morphology, and functions under precise control of external light irradiation [9]. This makes the photoresponsive patterned surfaces applicable in molecular motors and cell culture [10]. However, till now, studies on orthogonal photo-switching of micro/nano-patterned surfaces are lacking that develop the

[a] School of Optoelectronic Science and Engineering of UESTC, University of Electronic Science and Technology of China, No. 4, Section 2, North Jianshe Road, 610054, Chengdu, China.
[b] Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany. E-mail: wusi@mpip-mainz.mpg.de
[c] Department of Chemical and Materials Engineering, University of Kentucky, 177 F. Paul Anderson Tower, Lexington, KY, USA 40506.
† Footnotes relating to the title and/or authors should appear here.
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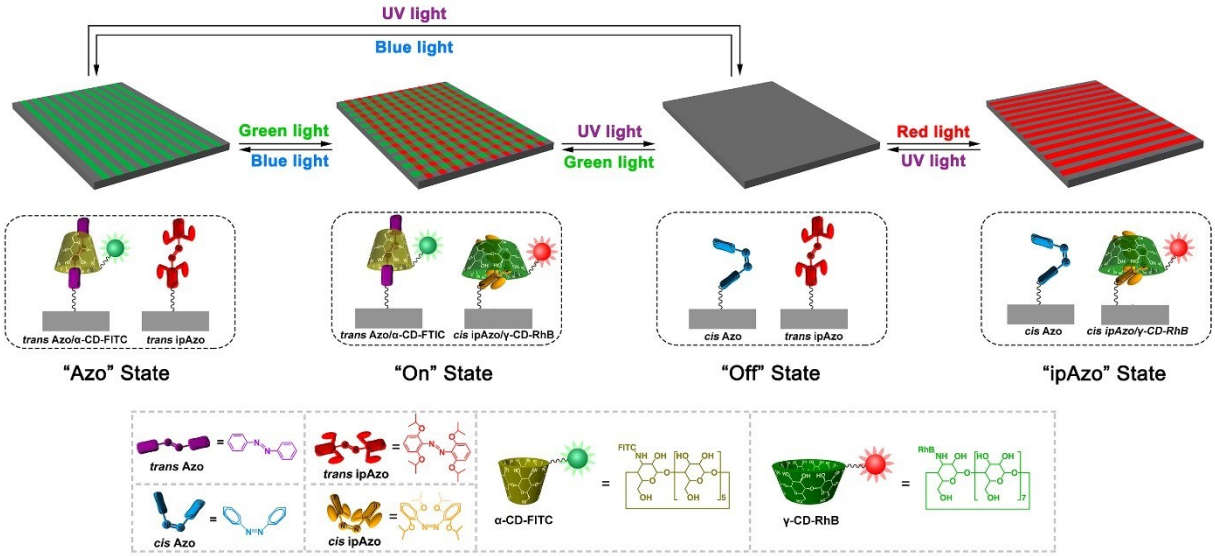

Scheme 1. Schematic illustration of photoresponsive orthogonal supramolecular micropatterned surface. 4 independent states on surface could be obtained and switched under controlling of UV, blue, green and red light irradiations.

surfaces to be intelligent and applicable in complex light environments. Herein, we show that 4 independent states of Azo/CD micropatterns are achievable by simply irradiating the surface with light of different wavelengths (**Scheme 1**):

1. "Azo" state: *trans* Azo/*trans* ipAzo, *trans* Azo/α-CD on surface;
2. "On" state: *trans* Azo/*cis* ipAzo, *trans* Azo/α-CD and *cis* ipAzo/γ-CD on surface;
3. "Off" state: *cis* Azo/*trans* ipAzo, no complex on surface;
4. "ipAzo" state: *cis* Azo/*cis* ipAzo, *cis* ipAzo/γ-CD on surface.

The orthogonally photo-controlled isomerization of Azo/ipAzo was investigated by UV/vis spectroscopy and ^{1}H nuclear magnetic resonance (NMR) spectroscopy (**Figure 1**). Azo-Si and ipAzo-Si were used as the model molecules and dissolved together (see Supporting Information (SI), **Scheme S1**). Our results demonstrated that Azo and ipAzo isomerization can be triggered in different directions by 4 light irradiations (**Table 1**). UV light at 365 nm excites the π-π* transition of *trans* Azo and triggers a *trans*-to-*cis* isomerization, inducing a sharp decrease of the π-π* transition band and an increase of the n-π* transition band (**Figure 1a**, **Figure S3a**). In contrast, the *trans*-to-*cis* isomerization of ipAzo under UV light irradiation is minimal. Only ~25% of *trans* ipAzo switched to the *cis* form after UV light irradiation (**Figure S3b**). Irradiation with blue light at 470 nm excites the n-π* transition and induces a *cis*-to-*trans* isomerization for both Azo and ipAzo (**Figure S4**). Green light (530 nm) induces a *cis*-to-*trans* isomerization for Azo, and *trans*-to-*cis* isomerization for ipAzo (**Figure S5**). Moreover, irradiation with red light at 625 nm triggers *trans*-to-*cis* isomerization of ipAzo, while Azo is not significantly affected (**Figure S6**). This might be attributed to the slightly higher absorbance of *trans* ipAzo than *cis* ipAzo in red light region (**Figure 1a**) [7, 11]. A summary of the photoisomerization of Azo and ipAzo under the different light irradiations is presented in **Table 1**.

The Azo/ipAzo combination can therefore be orthogonally controlled by light with various wavelengths, which was demonstrated by ^{1}H NMR. Azo-Si and ipAzo-Si with the same concentrations in DMSO-*d6* was used during the investigation (**Figure 1b**). After blue light irradiation, the Azo/ipAzo system was in the photostationary *trans* Azo/*trans* ipAzo state with approximately 100% and 96% of *trans* Azo and *trans* ipAzo, respectively (integral of ^{1}H NMR spectra). Green light irradiation transformed the system to the *trans* Azo/*cis* ipAzo while UV light irradiation transformed it to the *cis* Azo/*trans* ipAzo. Each of these photostationary states are easily obtained from any of the others by application of blue light (*trans* Azo/*trans* ipAzo), green light (*trans* Azo/*cis* ipAzo), and UV light (*cis* Azo/*trans* ipAzo). On the other hand, the fourth state (*cis* Azo/*cis* ipAzo) can only

Table 1. Photoisomerization of Azo and ipAzo under UV light, blue light, green light and red light irradiations.

	UV light	Blue light	Green light	Red light
Azo	*trans*-to-***cis*** [a]	*cis*-to-***trans***	*cis*-to-***trans***	Not affected
ipAzo	*cis*-to-***trans***	*cis*-to-***trans***	*trans*-to-***cis***	*trans*-to-***cis***

a. Text in bold and green indicates the photostationary state under the light irradiation.

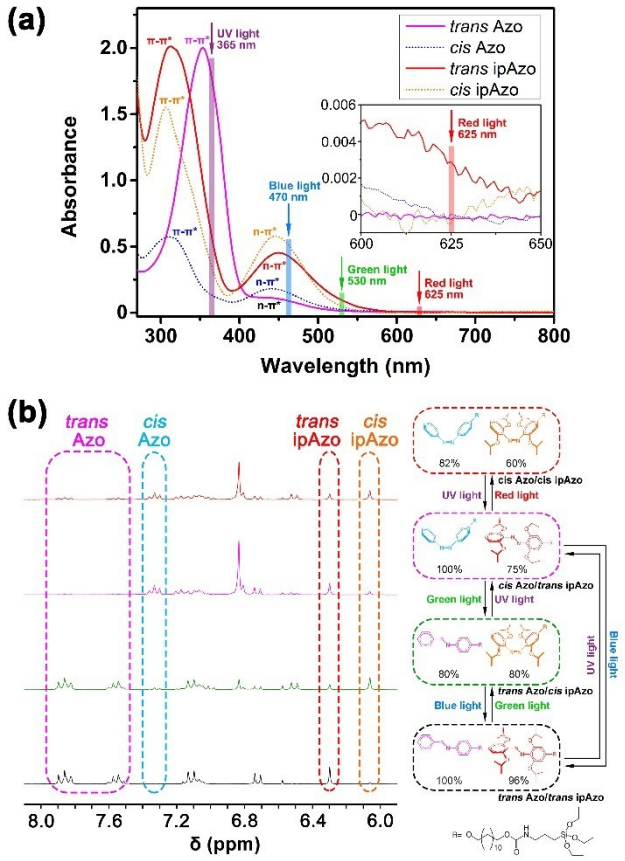

Figure 1. (a) UV/vis spectra of Azo and ipAzo ([Azo-Si]=[ipAzo-Si]=0.25 mM in dimethyl sulfoxide (DMSO)): *trans* Azo and *trans* ipAzo were obtained after heating at 60°C for 1 h in dark, absorbance of *trans* Azo at λ=351 nm and *trans* ipAzo at λ=310 nm were normalized; the UV/vis spectra of *cis* Azo and *cis* ipAzo were obtained from calculation (see detail in SI). (b) ^{1}H NMR spectra of Azo/ipAzo under UV, blue, green and red light irradiations ([Azo-Si]=[ipAzo-Si]=1.5 mM in DMSO-*d6*, 300 MHz at 298K. UV, blue and green light=30 min, red light=20 min.).

be achieved by starting with the *cis* Azo/*trans* ipAzo and irradiating with red light, which is reversible upon UV light irradiation (**Figure 1b**). The results obtained by ^{1}H NMR are consistent with our UV/vis data and **Table 1**.

To fabricate photoresponsive orthogonal micropatterned surfaces, Azo-Si and ipAzo-Si were micro-contact printed onto a glass surface (**Scheme S3**). A polydimethylsiloxane (PDMS) stamp with 3-μm wide stripes and 5-μm wide valleys was used for the micropattern preparation (**Figure S9**). Azo and ipAzo micro-stripes were immobilized on glass surfaces by printing, which are denoted as Glass-Azo and Glass-ipAzo, respectively (see detail in SI). The Glass-ipAzo was used to further prepare a photoresponsive orthogonal micropatterned surface, which is denoted as Glass-ipAzo/Azo. To prepare this pattern, an Azo-Si coated PDMS stamp was rotated by 90° and then stamped onto the Glass-ipAzo surface, which leads to a crossed grid of Azo/ipAzo micro-stripe structures (**Scheme S3**).

To visualize the microstructures, a green fluorescent dye, fluorescein isothiocyanate (FITC), was used to modify α-CD to obtain α-CD-FITC (**Scheme S2**, SI). The 2D fluorescent micro-stripes could be imaged by confocal microscopy on the Glass-Azo substrate after introducing an aqueous solution of α-CD-FITC, due to the formation of a host-guest complex between *trans* Azo and α-CD-FITC (**Figure S10a**). Irradiation by UV light leads to the disappearance of the fluorescent micro-stripes on the Glass-Azo surface. This is driven by the *trans*-to-*cis* photoisomerization of Azo, as described in **Table 1**, resulting in the dissociation of the host-guest complex, and further release of α-CD-FITC from the surface. The green fluorescent micro-stripes could be visible again on Glass-Azo surface by blue light irradiation and further treating with the α-CD-FITC aqueous solution (**Figure S10a**, **S11**, see detail in SI). As suggested by **Table 1**, the Glass-ipAzo could be controlled by green and blue light irradiation in an opposite manner (**Figure S10b**). To demonstrate this, a red fluorescent dye, rhodamine B (RhB), was modified with γ-CD to obtain γ-CD-RhB (**Scheme S2**, SI). Upon immersing the Glass-ipAzo substrate in a γ-CD-RhB aqueous solution in the dark, no fluorescent micro-stripes are visible due to the weak host-guest interaction between *trans* ipAzo and γ-CD-RhB. By irradiating the Glass-ipAzo substrate with green light and further treating with the γ-CD-RhB aqueous solution, 2D fluorescent micro-stripes become visible. This is attributed to the green light induced *trans*-to-*cis* isomerization of ipAzo on the surface (**Table 1**). While *cis* ipAzo shows a strong host-guest interaction with γ-CD, the γ-CD-RhB could be visualized on Glass-ipAzo surface. Furthermore, by irradiating the surface with blue light, the fluorescent micro-stripes can be erased (**Figure S10b**, **S12**, see detail in SI).

The Azo/α-CD and ipAzo/γ-CD host-guest complexes have been demonstrated to be orthogonal in our previous work [7]. Considering that the Azo/ipAzo system can be controlled by different light wavelengths to 4 different photostationary states, we demonstrated a photoresponsive orthogonal micropatterned surface using the Glass-ipAzo/Azo crossed micro-stripes described above (**Scheme S3**).

A mixed aqueous solution of α-CD-FITC and γ-CD-RhB (1:1, in molar ratio) was used for the orthogonal photo-switching process of Glass-ipAzo/Azo. The green fluorescent FITC and red fluorescent RhB can be monitored independently using different channels by confocal microscopy (SI). The Glass-ipAzo/Azo substrate surface was marked by a diamond cutter to make sure that the orthogonal photo-switching process occurred in-situ. Under blue light irradiation, the Glass-ipAzo/Azo surface is in the "Azo" state (**Scheme 1**). Fluorescent

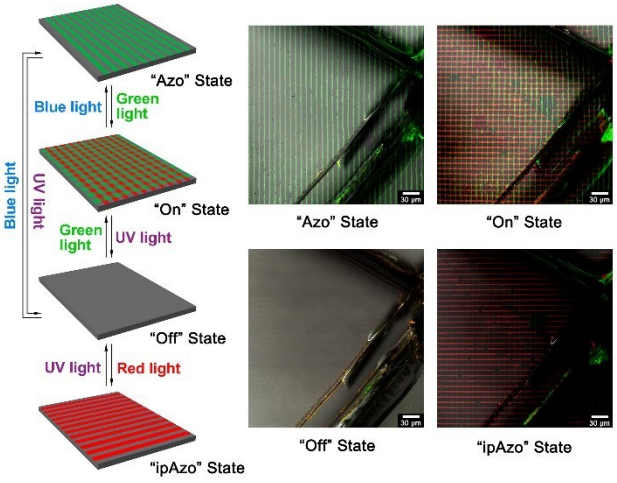

Figure 2. Confocal microscopic images of Glass-ipAzo/Azo after treating with UV, blue, green and red light irradiations. Scale bar: 30 μm.

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micro-stripes are therefore visible in the FITC channel after treating with the α-CD-FITC/γ-CD-RhB mixture (**Figure 2, S13**). Green light irradiation switched the Glass-ipAzo/Azo to the "On" state, both α-CD-FITC and γ-CD-RhB are thus immobilized on the substrate surface, and a crossed FITC/RhB micro-stripe structure is observed. Upon UV light irradiation, the Glass-ipAzo/Azo is transformed to the "Off" state, neither α-CD-FITC nor γ-CD-RhB are immobilized on the substrate surface. Therefore, no fluorescent micro-stripes are visible on the surface (**Figure S13**). Each of these states is easily obtained from any of the others by the application of blue light ("Azo" State, FITC micro-stripes), green light ("On" State, crossed FITC/RhB micro-stripes), or UV light ("Off" State, no micro-stripes) (**Scheme 1**, **Figure 2**), which are as expected by our UV/vis and NMR results. The fourth state ("ipAzo" State) is only obtained by irradiating the Glass-ipAzo/Azo substrate with UV light and red light in sequence; then the γ-CD-RhB is immobilized on the surface and fluorescent micro-stripes are only visible in the RhB channel (**Figure 2, S13**). UV light irradiation induces the back switching from the "ipAzo" state to the "Off" state. This demonstrates that the supramolecular micropatterned system, formed by the Azo/α-CD and ipAzo/γ-CD, can be photo-controlled orthogonally by UV light, blue light, green light and red light irradiation, and switched between 4 different states (**Scheme 1, Figure 2**).

In summary, we demonstrated orthogonal switching of an Azo/ipAzo system under pure photo-control by UV (365 nm), blue (470 nm), green (530 nm) and red light (625 nm) irradiation. 4 independent photostationary states of Azo/ipAzo combinations are realized and switched between each other by light. A photoresponsive orthogonal supramolecular micropatterned surface was fabricated by combining the Azo/α-CD host-guest complex with ipAzo/γ-CD. The successful design of photoresponsive orthogonal supramolecular systems offers more applications of light-controlled materials in complex irradiation environments. Although the reported structures are in the microscopic scale, we envision that photoresponsive orthogonal supramolecular systems should also be applicable to macroscopic systems. For example, Shi et al. proposed a novel methodology of macroscopic supramolecular assembly to fabricate 3D ordered structures [12]. This method can mildly load necessary bioactive species to designated locations within the structure during fabrication, which is significant for the increasing demand in constructing chemically or biologically specific tissue scaffolds. Our design may lead to more intelligent photoresponsive microscopic and macroscopic systems in the future.

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