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Multi-Addressable Photochromic Architectures: From Molecules to Materials

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Abstract:

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Multi-addressable architectures comprising light-responsive photochromic molecules and different stimuli-responsive components are appealing platforms for intelligent materials not only because of the potential diversity of components and corresponding properties, but also the functions resulting from their synergistic interactions. A variety of multi-addressable photochromic architectures are being designed to meet the demands of applications in different areas ranging from molecular machines to smart materials. This review highlights exciting recent advances in the field of multi-addressable systems that employ photoswitching molecules, specifically with regard to photo-/chemical-addressable, photo-/pH-addressable, photo-/thermal-addressable, photo-/redox-addressable, and multi-photo-addressable architectures. Design concepts, crosstalk between different components, and photoswitch integration in these multi-addressable systems are discussed.

1. Introduction

Design and fabrication of “smart” stimuli-responsive materials have attracted considerable attention due to their potential to significantly improve future technologies such as soft robotics,^[1–3] artificial muscles,^[4–6] sensors,^[7–10] drug delivery,^[11–13] and advanced actuator systems.^[14–17] These systems have been designed to respond to both a physical stimulus (e.g., light, electricity, temperature and pressure) and a chemical stimulus (e.g., solvent vapor, chemical analyte, and changes in pH). Among the various types of stimuli, light has multiple enabling advantages: (i) delivery of light does not require physical contact, allowing remote and non-invasive manipulation; (ii) light as a stimulus is both energy and material efficient, minimizing the generation of additional waste; (iii) light imbues inherent spatiotemporal control; (iv) the ability to independently control wavelength, mode, and polarization allows for multiplexing; and (v) light is typically orthogonal to other stimuli, allowing for the development of dual-responsive systems.^[18,19] In addition to these advantages, the emergence of optical technologies and instrumentation continue to provide various strategies for advanced light

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manipulation and delivery. Finally, the design and development of photo-switching molecules with improved properties (e.g., addressability, stability, modularity, efficiency and reliability), has helped revolutionize this field.

In recent years, a significant number of new photoswitches have been developed.^[20–27] A photoswitch is defined as a molecule that undergoes a reversible transformation on exposure to light.^[28] These are generally categorized into either P-type, wherein two distinct wavelengths of light are used to interconvert between two photostationary states, or T-type, wherein light drives the transformation to one photostationary state and heat drives the reversion. In both cases, the conversion between the two forms is usually accompanied by a significant property change. For example, azobenzenes have been used extensively for their shape change, resulting from the *cis-trans* isomerization upon irradiation, for various actuating applications.^[29–31] Similarly, hydrazones undergo a light driven isomerization between a stable *trans* configuration and a meta-stable *cis* configuration which have drastically different chelation and H-bonding properties.^[22,23] Spiroprans have largely been exploited for their transformation from a hydrophobic to a hydrophilic form with irradiation.^[20,32] Hemiindigos, which also interconvert between a *trans* and *cis* conformation, can have extraordinarily long thermal half-lives as high as 83 years at room temperature.^[24] Diarylethenes readily switch between two photostationary states, which have dramatically different optical and electronic properties, and show potential for memory and optoelectric applications.^[33] Incorporation of these photoswitches into a range of material architectures allows for strategic

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exploitation of their property changes and has led to breakthrough applications in many important research frontiers of materials science and life science, such as 3D printing,^[34] actuation,^[35,36] and light-controllable biomaterials.^[37] Investigations of smart materials bearing photochromic compounds and their light-responsive properties in single stimulus systems have been covered appropriately in the literature.^[19–21,33]

Multi-stimuli-responsive architectures that are sensitive to light and a second or more stimuli (e.g., chemical, thermal or redox) are materials of emerging interest. Compared with single stimuli systems, multi-addressable systems are more capable of sophisticated functions and complex behavior due to the interplay between different stimuli. When multiple stimuli can be synergistically addressed, there is often a significantly larger benefit as compared to the sum of analogous systems using a single stimulus.^[38–40] Herein, we highlight recent examples of research advances using multi-addressable systems (**Scheme 1**). This review is broken down into six parts: (i) photo- and chemical-addressable architectures; (ii) photo- and pH- addressable architectures; (iii) photo- and thermal-addressable architectures; (iv) photo- and redox- addressable architectures; (v) multi-photo-addressable architectures; and (vi) photo- and less common stimuli- addressable architectures. We focus on multi-addressable system that leverage photoswitches as one of their key design features. For each section, we highlight applications in soft materials that demonstrate the potential of these multi-addressable photochromic systems. We exclude multi-addressable systems that don't contain a photo-switching molecule as they have been reviewed elsewhere.^[38–44]

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2. Introduction to Commonly Used Photoswitches for Multi-Addressable Systems

Photoswitches undergo reversible photoreactions to interconvert between two photostationary states, potentially over many cycles. Their switching process usually involves reversible electrocyclization of a π -system (spiropyran, diarylethene, donor-acceptor Stenhouse adducts and dimethyldihydropyrene)^[20,27,33,45,46] or *cis-trans* isomerization (azobenzene, hemiindigo and hydrazone)^[22–24,29] (Figure 1).

Azobenzene is an almost ideal component for a range of molecular devices and functional materials owing to its wide availability, ease of synthetic modification and tunable absorption spectrum. Through rational structural modification, azobenzenes with absorptions that range from UV to near-IR region have been synthesized.^[30,47–49] Adding to this wavelength tunability, certain azobenzenes can also modify their absorption properties with pH.^[50,51] Due to the wavelength tunable properties and ability to switch in an aqueous environment, azobenzene represents a privileged scaffold for systems relying on wavelength control. In addition, the change in geometry and/or polarity upon isomerization of azobenzenes modulate interactions to dictate the structure of bulk materials (ex. hydrogel, nanoparticles, polymers),^[52–54] orient surrounding molecules (ex. liquid crystals and polymers) to perform a task,^[55–58] or to modify the activity through conformational changes.^[59,60] Thanks to these properties, azobenzenes are widely utilized as a light-triggered switch in a variety of actuators, polymers, surface-coatings, molecular machines, molecular logic gates, and metal ion

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chelators. Hemithioindigo also undergoes a similar *cis-trans* isomerization as azobenzenes and thus holds great promise. Interestingly, their photoisomerization can proceed with visible light, which is beneficial for applications not tolerant of high energy UV light.^[24] Hydrazone is an emerging family of switches due to their straightforward synthesis, functional diversity, tunability, and stability.^[23] The bridging imine bond undergoes stimuli-responsive *cis-trans* isomerization by either light activation or chemical modulation (typically via pH changes). This dual control over isomerization is a unique feature of the hydrazone functional group and makes it a versatile tool for multi-stimuli architectures.

Spiropyrans, another well-studied family of photochromic compounds, undergo a heterolytic C–O bond cleavage and change from closed spiropyran (SP) form to open merocyanine (MC) form with a range of stimuli, including light, metal ions, acids and bases, and mechanical force.^[61–64] As MC possesses a planar conformation with extended π -conjugation, the optical properties of SP and MC differ substantially upon photoconversion, which has enabled this class of photochromic material to be employed as visual sensors. In addition, significant charge separation occurs upon conversion from SP to MC forms, thus giving rise to a photoactivated change in dipole moment. This change in dipole moment of SP due to light irradiation has been exploited in many systems to reversibly control polymer solubility,^[65] emulsion formation,^[66] and surface wettability.^[67] Another important property of SP and MC forms is that they have different affinities for protons and thus can be used as a light-activated photoacid. In the MC form, the phenoxide anion can be stabilized through

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electronic conjugation within the molecule. As the proton affinity is consistent with the stability of the photoisomers, light-controlled acidity change can be realized by the isomerization of SP. Several SP based photoacids have been designed by Liao,^[68–72] Heckel^[73] and our group.^[74] These have been integrated with different proton-responsive moieties, such as acid-catalyzed chemical reactions, hydrogen bond modulation, light-controlled polymerization, and self-assembly.^[75] In addition, the MC form also feature higher affinity towards other chemical species, such as metal ions, enabling capture/release functionalities upon irradiation.^[63]

Diarylethenes, most commonly dithienylethene (DTE), undergo photoisomerization between a π -conjugated closed state and a non-conjugated open state. These two forms display dramatically different optical and electronic properties. Because significant absorption shifts from UV region (\sim 250–330 nm) to visible light region (\sim 500–700 nm) are observed for diarylethenes upon photocyclization, they function as efficient photo-responsive energy acceptors in energy transfer process when coupled with fluorophores.^[25] Since the first on/off fluorescence photoswitch based on the fluorescence resonance energy transfer (FRET) mechanism using diheteroarylethenes as acceptors was reported by Jares-Erijman and coworkers in 2002,^[76] many others developing sensing and logic gates have leveraged this diarylethene-based photo-addressable fluorophores approach.^[33] In related work, as the non-conjugated open and the conjugated closed forms of diarylethene also have quite different electronic properties, they have been integrated with electrochemical-responsive components for dual switchable organic electronic devices, especially with regard to

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photo- and redox- switching of conductance.^[77,78] Diarylethenes are thus key building blocks for architectures with photo-controllable optical or electronic properties.

Negative photochromes, which feature conversion of a colored thermodynamically stable isomer to a decolored isomer, have recently gained interest in the field due to enhanced penetration during irradiation. Donor-acceptor Stenhouse adducts (DASAs) represent a new class of visible and near-infrared light-activated negative photochromic molecules developed by our group.^[79-83] They exhibit colored-to-colorless changes and also polarity alteration during open/closed isomerization. By tailoring the acceptors (Meldrum's, barbituric acid, or carbon acid) and donors (secondary alkyl amine or aniline), an absorption range spanning from 450 nm to 750 nm has been achieved. Due to the tunable optical properties of different DASA derivatives, wavelength-selectively multi-photo-switchable DASA systems and functional polymer materials have been developed. In addition, DASAs have very little absorption between 300 and 500 nm, resulting in minimal absorption overlap with known privileged photoswitches such as azobenzenes. This property enables independent addressability when different families of photochromic compounds are integrated into a single system.^[84] Similar to DASAs, photochromic systems based on dihydropyrene (DHP) form the thermodynamically less stable and colorless cyclophanediene isomers (CPD, open form) with visible light irradiation. Recently, quantitative photoconversion between both photo-states was achieved in this photochromic system,^[45,46] which will hold great promise for multi-addressable systems.

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Given the plethora of fascinating structural, electronic, and/or optical property changes enabled by the library of photoswitches described above, as well as their orthogonal compatibility with non-light mediated stimuli, it is not surprising that the field of multi-stimuli responsive materials has seen tremendous advances. However, we believe the potential for controlling complex behavior using photoswitching building blocks is still at the beginning of this emerging field.

3. Photo- and chemical- addressable architectures

Work in the field of photo- and chemical- addressable architectures has largely been motivated by the demand for increased information density, with the goal of manipulating molecular logic.^[85] Inspired by the fact that information is transported, processed, and retained by molecular substrates in living organisms, molecular logic—with its nanoscale size, low power consumption, and good performance—presents an attractive opportunity for next generation information processing technologies. Molecular switches or logic gates are a kind of organic molecules which can change their states (structurally and functionally) in response to chemical, electrical, or optical inputs. Accompanying this change in state, a chemical, electrical, or optical output is also produced.^[86] These molecules with two distinct and reversible states can then be used as elements of logic systems to perform various operations. Stemming from this body of work dealing with molecular switches and logic gates, more recent efforts have turned to coupling photochromic molecules with various other functional units (especially those responsive to acid/base, solvents, ions, etc).^[87–92] Similarly, strategic design of the linkage between different units has enabled elegant input/output

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transduction mechanisms, such as photochromism, energy transfer, and fluorescence quenching, to be employed for logic gates with complex functions.

In a recent example, Pu and coworkers synthesized a novel fluorescent switch with diarylethene and rhodamine B units linked by a triazole group (**10**) (**Figure 2**).^[93] In this structure, the rhodamine B unit serves as a “naked-eye” chemosensor. Although typically colorless and nonfluorescent, the rhodamine unit of this switch is responsive to protons or metal ions (Al^{3+} or Cu^{2+}), and isomerizes to the ring-open forms **10'**, **10-Cu²⁺** and **10-Al³⁺** respectively, turning a pink color and exhibiting strong fluorescence. The emission band of rhodamine in the ring-open state spans from 550 to 700 nm, which overlaps with the absorption band of the closed form isomer of the diarylethene unit. Subsequently, when the diarylethene derivatives **10'** were exposed to UV light and isomerized to **1C'**, the emission of rhodamine at 595 nm decreased substantially due to the photoisomerization of the diarylethenes by energy transfer. In this logic circuit, using either light (UV and/or visible) and a chemical input (acids, bases, and metal ions), the fluorescence intensity of **10** as an output signal could be selectively tuned.

In the above example, the energy transfer process between different functional units is crucial for the design of a combinational logic circuit. In some cases, selective individual addressability of coexisting subunits in a single molecule is highly desirable. Here, the interaction between subunits, such as energy transfer and electronic coupling, is not favorable as it leads to loss of control in the

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process. Thus, rational choice of selectively switchable components and their linkages is paramount. Delbaere and coworkers synthesized a dithienylethene (DTE) linked to an indolino[2,1-b]oxazolidine unit **2** (Figure 3).^[94] This DTE photoswitch (**2**) undergoes cyclization/opening upon irradiation; concurrently, the benzazolo-oxazolidine component can switch between open and closed forms in response to small molecule acids and bases. As presented, the system has 8 (2^3) unique isomeric states through *cis-trans* isomerization with light, heat, and chemical stimuli. By adding trifluoroacetic acid (TFA) vapor, the oxazolidine ring in **2-I** opens immediately, and results in the protonated open form **2-II**. This **2-II** can revert back to **2-I** with addition of triethylamine. When state **2-II** is irradiated by light with wavelength longer than 352 nm at low temperatures, the *trans-cis* isomerization of the ethylenic junction occurs, producing state **2-III** (up to a 90% conversion yield). In this conformation, ring-closing of the DTE subunit is inhibited. State **2-III** can revert back to **2-II** through thermal relaxation at ambient temperature. With treatment of triethylamine, ring-closing of the benzazolo-oxazolidine unit of **2-III** happens, thus forming state **2-IV**. When **2-IV** is irradiated with 254 nm light, the **2-V** state with a DTE unit in its cyclized form is generated (with a photostationary state of 90%). State **2-V** can 100% transform to **2-IV** with visible light irradiation. Conversion of **2-V** to **2-VI** occurs on exposure to TFA at low temperature. The hindered *cis*-form **2-VI** is thermally unstable and relaxes to the more stable *trans*-form **2-VII**, which can be converted into **2-VIII** by the addition of base. With visible light irradiation, the DTE unit in state **2-VIII** ring-opens, completing a full octa-state cycle with the return to the initial state **2-I**. This impressive hybrid-switch system exhibits eight unique and interconvertible isomers, making it one of the most complex multi-addressable molecules known to

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date. Aside from ions and acid/base, solvent and other chemicals have also been coupled with photo-responsive molecules to construct multi-addressable switches or logic gates. Klajn and coworker have designed gold nanoparticles functionalized with both azobenzene- (UV-sensitive) and diamine- (CO₂-sensitive) terminated ligands.^[94] Aggregation of the gold nanoparticles occurs only when both UV light and CO₂ are applied simultaneously, thereby effectively functioning as an AND logic gate.

In addition to these molecular logic gates, photo- and chemical- addressable soft materials have also been designed. Tian and coworkers constructed a novel three-component gel system that could undergo a light-induced gel-sol transition behavior (**Figure 4**).^[95] In their work, they synthesized a bisthiénylene with aza-15-crown-5-ether group (**3**) that could reversibly capture and release calcium ions by using UV and visible light to modulate the bisthiénylene unit. When **30** was doped into a two-component organogel containing calcium ions and lecithin, the crown ether efficiently sequestered the calcium ions, transforming the initially dark blue gel to a light blue fluid. Upon UV irradiation, the closed isomer **3C** was formed, causing the crown ether to release the calcium ions thereby regenerating the initial organogel. It is well known that crown ethers can coordinate with metal ions to form supramolecular networks, but to achieve a sol-gel transition would necessitate tedious removal of the ions from the system. Here, the integration of a photoswitch enables ready access to a complex behavior that would be otherwise difficult to obtain.

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Incorporation of photoswitches and other chemical-responsive units into supramolecular self-assembling systems is another efficient way to achieve high complexity and adaptivity in soft materials. Aida and coworkers developed a photo-reconfigurable bionanotube by taking advantage of Mg^{2+} -induced supramolecular assembly. In their work, a mutant barrel-shaped chaperonin protein functionalized with multiple photochromic **4-SP** units was synthesized (**Figure 5**).^[96] The nonionic **4-SP** units on protein isomerize to the ionic **4-MC** form with UV light irradiation. In the presence of $MgCl_2$, the ionic **4-MC** units coordinate with Mg^{2+} and form multiple $MC \cdots Mg^{2+} \cdots MC$ bridges, connecting the monomeric protein into a stable supramolecular nanotube. When subjected to visible light, the reverse isomerization of **4-MC** to **4-SP** occurs which breaks down the $MC \cdots Mg^{2+} \cdots MC$ bridges resulting in the dissociation of the nanotube structure. The formation and dissociation process of these nanotubes is completely reversible, responding both to light irradiation and the presence of Mg^{2+} ions. Biological systems tend to be chemical responsive by default, but as seen here, incorporating photoswitches allows for the nature of that response to be modulated with light stimulation, resulting in systems with more complex behavior and a higher degree of control.

Nature often serves as a source of inspiration when studying novel multi-stimuli-responsive materials. Schenning and Priimagi groups sought to mimic the behavior of nocturnal flower by developing a liquid crystal network actuator whose mechanical motions are dictated by light and water exposure (**Figure 6**).^[36] The composition of the actuator is shown in **Figure 6b**. The azobenzene derivative Disperse Red 1 acrylate **5** behaves like a “photothermal moiety” while acrylate-based

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carboxylic acid units are sensitive to humidity, due to their hydrogen bonding interactions. Under dark and humid conditions, water can selectively absorb onto the “flower petal” causing the material to swell thereby opening the “flower”. Increased light irradiation and decreased humidity causes de-swelling which results in the closing of the actuator. Alongside this work, Naumov and coworkers have reported hybrid-systems based on agarose materials with acidochromic fluorophores or derivatives of azobenzene that undergo similar humidity- and light-induced movements.^[97,98] Yu and coworkers reported photo- and hydro- induced mechanical actuation of a hydrophobic, porosity-free crosslinked liquid crystals polymers film through hydration of the hydrophilic carbonyl and ether groups and photoisomerization of azobenzene chromophores within the liquid crystals.^[99] While water may not immediately come to mind as a stimulus, these and various other examples demonstrate that simple processes (ex. swelling/de-swelling) can be partnered with photochromic compounds to create elegant systems with biomimetic-like behaviors.

These investigations of photo- and chemical- addressable architectures are critical in laying the foundation of future molecular logic-based devices, responsive organogels, supramolecular assemblies and other soft materials. From a design standpoint, the most common operation for these molecular switches and logic gate employ chemical signal inputs and optical outputs, making these systems attractive for the future development of chemosensing, medical diagnostics, and smart materials. However, multiple challenges have yet to be satisfactorily addressed, creating a demand for further investigation in this space. One primary drawback of these systems is the

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addition of chemical species to trigger the process, which leads to buildup of chemical waste after several cycles of operation. This chemical requirement then imposes limitations on both the cyclability and the nature of the surrounding medium of the molecular switches and logic gates. In moving forward, waste management of these chemically activated systems and “clean” fuels will require further development.

4. Photo- and pH- addressable architectures

Considering the waste management problem of photo- and chemical- addressable architectures, there was interest in developing systems that use “clean” stimuli that would circumvent chemical accumulation. In fact, nature already provides one potential answer. Biological proton pumps generate differences in proton concentration across a lipid bilayer by light-driven processes. In this way, light energy is converted to a chemical output. With regards to chemical waste, one might imagine that we can emulate nature’s efficiency and cleanliness by using light to drive these chemical processes. To date, photoacid generators^[100] and photoacids^[71] have been the main classes of molecules for generating protons with light irradiation. Photoacid generators, for example, triphenylsulfonium salt 4-(methacryoxy)-2,3,5,6-tetrafluorobenzenesulfonate, undergo a decomposition mechanism and release a proton by a combination of light and heat. Usually, these molecules are salts, comprising a photo-sensitive cation which decomposes upon irradiation and an anion which serves as the conjugate base to the resulting acid product. Due to the nature of their

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mechanism, photoacid generators are generally irreversible. Conversely, photoacids are molecules that reversibly undergo proton photo-dissociation and thermal reassociation. Photoacids based on photochromic molecules with promising reversibility that have been reported are mainly comprised of spiropyran and azobenzene derivatives. For example, merocyanine based photoacids with long disassociation lifetimes and reversible pH change (as much as 2.2 units) were recently developed by the Liao group.^[71] The Liao group and recently our group have been working on further development of several photoacids compatible in a range of different environments, from aqueous buffer solutions^[72] to organic solvents,^[68,74] to meet demand for applications in different areas. Azobenzene derivatives are another type of photoacid that take advantage of photochromic switching. For example, the *cis-trans* photoisomerization of 2-hydroxyazobenzene causes a significant pK_a change in the phenol group, enabling acid driven oscillations by single-wavelength illumination.^[101] These “two birds, one stone” photoacids exploit the photo-switching capability of photochromes, enabling both proton capture and release, and are thus ideal candidates for controlling numerous proton-driven processes by light manipulation. As such, numerous applications of photoacids have been demonstrated, including acid-catalyzed reactions,^[71] controlled self-assembly of nanoparticles,^[75] molecular machines,^[102,103] formation of hydrogels,^[104] anti-bacterial materials,^[70] ion sensing.^[105]

In using photoacids to drive chemical processes, the issue of chemical accumulation of side-products is largely eliminated. Aprahamian and coworkers successfully demonstrated that the proton generated by a merocyanine photoacid could be used to reversibly switch a hydrazone-based pH-

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sensitive switch **6**.^[106] When an aqueous solution of **7-MC** derivative and triethylene glycol monomethyl ether functionalized hydrazone switch was irradiated with 430 nm, a photostationary state of **6** was reached after 5 minutes as shown in **Figure 7**. With a 2:1 molar ratio of **7-MC** derivative to hydrazone switch **6**, more than 90% conversion was achieved. The thermal ring-opening of **7-SP** returns the system to its initial state in less than an hour when left in the dark. The system was found to be very robust and was demonstrated to be recyclable up to 20 times without deleterious waste production, and as many as 100 times in methanol.

Photoacids feature good reversibility, which is a critically important property for applications such as erasable imaging and controlled drug delivery. In this context, Klajn and coworkers describe a conceptually novel approach for reversibly assembling nanoparticles (NPs) using light.^[75] The approach is novel in that it does not require that the particles themselves be functionalized with light-responsive moieties. Instead, this strategy uses photoacids to locally modulate the interparticle interactions. Here, Au NPs functionalized with 11-mercaptopundecanoic acid were prepared (**Figure 8**).^[75] The NPs were insoluble in methanol, presumably because of multiple hydrogen bonds between the pendant carboxylic acid groups. These hydrogen-bonding bridges can be broken down by addition of strong acid, such as HCl, resulting in a stable particles suspension. When **8-SP** was added to the acid-stabilized Au NPs suspension, because of its high pK_a relative to HCl, it behaves as a base and competes with the tethered carboxylic acid groups for protons. Thus, the light-induced proton capture and release of **8-SP** dictates the ligand interactions between NPs, realizing the

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reversible control over the assembly of non-photo-responsive NPs with light. Color change during the assembly/disassembly sequence of the Au NPs was also exploited to create a re-writeable imaging system. When all the reaction components were incorporated into a crosslinked poly(ethylene glycol) gel. Initially, the gels are yellow, indicating that the photoacid was sitting in the protonated **8-MCH**⁺ form; after irradiating the gel with blue light through a mask, the exposed regions turn red, indicating the conversion of the photoacid to the colorless **8-SP** form and NP dissolution. Upon removal of the light source, the created patterns disappeared as the gel returned to its initial yellow state. This system is remarkably robust, showing no loss in performance even after 100 write-erase cycles, enabling their potential applications in reversible, time-sensitive information storage.

Aside from imaging, this ability to adjust pH with spatiotemporal resolution is highly desirable in application areas such as soft matter generation and patterning. Eelkema and coworkers employed a photoacid as a light-switchable catalyst to spatially control the assembly of synthetic molecular fibers (Figure 9).^[104] Low molecular weight gelators can be generated by an acid-catalyzed reaction of cyclohexane trishydrazide with three equivalents of aldehyde. Here, water-soluble photoacid **7-MC** was used, which drives a pH value drop from 6.6 in aqueous solution ($[7-MC]=1.0$ mM) to 5.4 with visible light irradiation in less than 2 minutes. The pH of the solution returns to its original value within 5 min in the dark. When an aqueous solution containing cyclohexane trishydrazide, aldehyde, and **7-MC** was irradiated with visible light ($800 > \lambda > 400$ nm), a pale yellow, stable gel was obtained.

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Compared with the maximum storage modulus (11.7 kPa) of non-irradiated samples, a substantial increase was observed in the irradiated samples (18.5 kPa). The sample without **7-MC** only reached a maximum modulus of 6.9 kPa. These results confirmed that **7-MC** catalysts accelerate the formation of gelators which also accelerates the formation of the gels and results in more rigid gels. By this same mechanism, gel patterning and local modulation of mechanical properties can be achieved by selective light irradiation. Using simple masks, the authors demonstrated controlled gelation only in the areas that were irradiated. This result illustrates controlled formation of soft materials such as hydrogel and micropatterns by taking advantage of spatial control with light-switchable catalysts.

In this section, only a few examples were selected to illustrate the recent exciting progress of photoacids. The range of available property changes have enabled these systems to find applications in actuation, biological manipulation, as well as the aforementioned imaging and patterning. However, one limitation in these reversible photoacids is the limited change in pH. While photoacid generators typically produce acids with pK_a values of strong acids, photoacids operate in the weak acid range. There are significant synthetic difficulties in designing a strong acid reversible photoacid but doing so would be hugely enabling and broaden the scope for these photoswitches substantially. Because of the ubiquity of acid-catalyzed reactions and acid-responsive materials, it is clear that photoacid-incorporated smart materials will be of increased interest in the coming years.

5. Photo- and thermal- addressable architectures

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Thermal-responsive materials have emerged as one of the most extensively studied stimuli-responsive systems, with numerous applications including drug delivery,^[107] nanopores,^[108] and actuators.^[109] There are many well-studied thermal-responsive polymers and thermally controllable chemical reactions.^[110,111] Coupling these classic systems with more novel photochromic compounds is an efficient way to design photo- and thermal- dual-mode addressable systems. Poly(N-isopropylacrylamide) (PNIPAM) is among the most well-behaved thermal-responsive polymers. In aqueous solutions, PNIPAM spontaneously aggregates when the temperature goes above the lower critical solution temperature (LCST). This characteristic behavior of PNIPAM enables its use as a 'smart' component in thermally responsive material systems. Branda and coworkers designed an amphiphilic photochromic polymer **9-P1-o** with a hydrophilic PNIPAM backbone with P-type hydrophobic dithienylethene (DTE) photochromic units pendant from the backbone (**Figure 10**).^[112] When these **9-P1-o** copolymers were added to aqueous solutions, they spontaneously self-assemble to form nanoparticles. When exposed to light and thermal stimuli, the hydrodynamic diameter of the nanoparticles could be interconverted between two distinct stable states. It is believed that this change is largely driven by the reversible swelling of H₂O into the **9-P1-o** nanoparticles. Additionally, it is known that the pendant DTE groups photo-isomerize into a more rigid ring-closed form, which seems to be responsible for their increase in diameter after irradiation with 313 nm light (**9-P1-pss**). Because the LCST doesn't involve any high energy states and the photoisomerization of DTE is

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known to be stable, the reversible changes in diameter can be cycled with no observable degradation in performance. Many polymers have LCSTs as well as UCST (upper critical solution temperatures), making this a fairly generalizable strategy for incorporating photoswitches into systems with fully orthogonal mechanisms.

The thermally reversible Diels–Alder reaction is another well-known method for imbuing dynamic thermal-responsive properties in materials and has been extensively employed for self-healing materials.^[113] This thermally activated reaction works in the absence of catalyst and generates no byproducts, while producing stable covalent crosslinks even at mild conditions. Recently, investigators have begun integrating these Diels–Alder reactions into photo-addressable systems to access materials with another degree of control.^[114,115] For example, Hecht and coworkers developed photo-switchable furans with diarylethene unit **10** that can modulate the rates of formation/dissociation of Diels–Alder adducts with maleimides. With this system, reversible crosslinking and de-crosslinking of polymer network can be achieved with spatiotemporal control.^[116]

As shown by a model scratch in **Figure 11b**, at temperatures above 120 °C, the polymer material spontaneously heal as internal Diels–Alder reactions reform the network. Interestingly, due to the electronic influence of the photo-switchable furans, the healing capabilities are significantly suppressed when the films were irradiated with UV light, and then fully recovered with visible light illumination. Again, because of the stable and reversible chemistries at play in this system, the changes could be cycled with high retention of performance. This example took a classic thermally

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self-healing motif (Diels–Alder chemistry) and synthetically integrated it with photoswitches that enabled the modulation of the self-healing behavior with light stimulation. In their more recent work, a series of new photo-switchable bis-furyl-substituted diarylethene crosslinkers with different spacer lengths were fabricated to investigate their influence on healing properties of a similarly constructed polymer network.^[117] With these crosslinkers, the temperature required for the retro Diels–Alder reaction to occur, thereby de-crosslinking the network, is further decreased as compared to the original photo-switchable furan-based crosslinker. With the variety in photoswitches' electronic and photophysical properties, this same concept of modulating a reaction by coupling a thermally responsive unit with a photoswitch has enumerable variations.

However, one distinct limitation in thermal- and photo- addressable architectures is in the choice of photoswitch. Because heat is being used as a stimulus, T-type photoswitches are rendered less effective as their thermal relaxation cannot be decoupled from the response of the other thermal-addressable unit. For this reason, T-type azobenzene and similar switches, despite their significant property changes and high performance, can be difficult to integrate well in systems with dual thermal- and photo- responses. While clever implementation may allow some workarounds for this limitation, in general P-type photoswitches are intrinsically better suited to achieve orthogonal control of photo- and thermal- addressable architectures.

6. Photo- and redox- addressable architectures

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For systems requiring fast and efficient operation with minimal interference, photons and electrons are amongst the most desirable stimuli. Both light and electrical potential can be applied by an outside source, with minimal physical perturbation, at exponentially faster rates than the diffusion of chemical or thermal stimuli and can be removed just as quickly. When redox-responsive compounds, such as transition metal complexes, are integrated with photochromic molecules, they can substantially influence the photochromic properties and further endow new properties and functions to the system. Until recently, modulating photophysical properties, such as absorption and luminescence, had been the primary focus of photo- and redox- addressable architectures. Nishihara and coworkers have worked to incorporate various photochromic molecules with common redox-active ferrocene systems. For example, facilitated by the reversible redox reaction between Fe(II) and Fe(III) of ferrocene, a reversible *trans-cis* isomerization cycle for meta-ferrocenylazobenzene using only green light (546 nm) was achieved by taking advantage of a metal-to-ligand charge transfer.^[148] This is a notable achievement, as it eliminates the need for harsh UV light to revert the azobenzene to its original conformation, thus creating a more stable and reversible system. When a spiropyran was similarly functionalized with a ferrocene complex, it exhibited reversible tuning of the lifetime of the metastable merocyanine form based on the oxidation state of the attached ferrocene/ferrocenium redox process.^[119] This second degree of control allowed for the researchers to modulate the redox-active photochrome between two states: one with high reversibility (shallow memory) with a Fe(II) metal center, and one with much higher stability (deep memory) when the

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metal center was oxidized to Fe(III). Zhu and coworkers have demonstrated a photo-switchable triad system containing three functional components: a photochromic diarylethene unit, a naphthalimide-based chromophore, and a redox-responsive ferrocene.^[120] When the photochrome core of this triad is in its ring-open form (anti-parallel) and the metal center is Fe(II), the efficiency of the ring-closing photoisomerization is incredibly low, at less than 1%. Upon chemical or electrochemical oxidation to Fe(III), the efficiency of the photoisomerization jumps to 22%, demonstrating redox-gated photochromism. Additionally, the fluorescence of naphthalimide chromophore can be switched off/on with the reversible redox of ferrocene by a photo-induced electron transfer pathway. Thus, the authors demonstrated the use of a photoswitch to construct a triad system whose photophysical properties can be modulated by light, chemical, and electrochemical stimuli. Other metal complexes, such as cobalt and ruthenium complexes, also exhibit good redox properties that can be integrated with photochromic molecules to form functional systems.^[121,122] Recently, Royal, Cobo, and coworkers have designed a dimethyldihydropyrene-pendant cobalt complexes $\text{Co}^{\text{II}}(\text{L}_c)_2^{4+}$ **11** (Figure 12).^[122] This complex (**11**) exhibits four distinct states (“quadri-state”) between which it can interconvert with redox- and photo- stimuli. First, with light irradiation and or heat, the dimethyldihydropyrene-containing ligands, L_c^+ , can reversibly isomerize from a closed-ring form to open-ring form, which have very different absorption properties. At the same time, the complexed Co^{II} center can reversibly switch between its different redox states, $\text{Co}^{\text{II/I}}$ and $\text{Co}^{\text{III/II}}$, without interfering with the electrochemical behavior of the L_c^+ ligand. Thus, interconversion between four distinct states was achieved for **11** via strategic use of optical, thermal, and electrochemical inputs.

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The unique ability to modulate photophysical and electrochemical properties in photo- and redox-addressable systems is of great interest for a variety of applications, including fluorescence switches, molecular photo memory devices, and molecular logic gates.

Recently, systems composed of two or more π -conjugation systems, based on the dithienylethene (DTE) moiety, have garnered particular interest for their multi-state switching properties, which have potentially powerful implications for the future of molecular electronics.^[121,123,124] However, it is difficult to access all possible ring-open/-closed isomers in electronically delocalized systems due to internal competing energy transfers. Integrating ligands with multiple DTE units into electrochemically active metal-coordinated systems has been found to be an effective method for achieving stepwise photochromic reactions by reversibly changing oxidation states. Chen and coworkers fabricated a system for the electro- and photo-commutation of molecular transport junctions using on-wire lithography-generated nanogaps (about 5 nm) modified with a trimetallic complex containing two DTE units, **12** (**Figure 13A**).^[123] Both DTE units isomerize between a π -conjugated state (closed) and a non-conjugated state (open) with light irradiation, thereby dictating the conductivity of the nanodevice. As shown in **Figure 13B**, the DTE molecules can isomerize between the fully π -conjugated **12cc**, which has low resistance, to the non-conjugated **12oo**, with high resistance. This transformation is driven by visible light (700 nm) or UV light irradiation, leading to conductivity decreases and increases, respectively, of the **12**-based nanodevices. Beyond the one-step light-driven modulation of conductivity, this system demonstrated stepwise and orthogonal

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switching of the conductivity of the nanodevice (via stepwise activation of the two DTE units) with electro-chemical and/or light stimuli. Enabled by this orthogonal control, these multi-addressable molecular transport junctions-based nanodevices can be utilized for various logic operations. Related research has also been conducted by the Rigaut and Chen groups.^[121,124] These multi-addressable systems provide a solid foundation for the development of smart molecular devices, but are currently limited by their fabrication and operative conditions. The synthetic difficulty in producing more resilient and robust molecular junctions on scale with practical applications poses a significant challenge to be addressed.

Another main research interest for photo- and redox- addressable architectures is in their application as molecular machines. It is well documented that light irradiation and redox processes can be used to control molecular recognition and conformational changes.^[125] In molecular machines, photochemical and electrochemical techniques are both employed not only to induce chemical or conformational changes, generating quasi-mechanical movements, but also as elements of more complex systems. Integration of photo- and redox- responsive components together has proven to be an effective method for generating molecular machines with more complex functionalities. Credi, Stoddart, and Venturi demonstrated a system whereby integration of photo- and redox- responsive units enabled the operation of a [2]rotaxane as a bistable memory element.^[126] Using electrochemical stimulus to oxidize the tetrathiafulvalene unit, the conformation of a neighboring rotaxane could be controllably switched between two states, constituting a molecular switch

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capable of storing data. This data could then be locked by using UV irradiation to isomerize the bridging azobenzene unit to a *cis* form, trapping the rotaxane unit in the chosen conformation as shown in **Figure 14**. The oxidized unit can then be selectively reduced back to its initial oxidation state without losing the stored data. Finally, the entire system could be heated or irradiated with visible light to erase the data and reset to the initial state. This work utilized light and redox stimulation synergistically to create a complex molecular switch with orthogonal write/erase and lock/unlock functionalities. One notable benefit of the choice of stimulus is the speed and efficiency of the transformations, as well as the mild operating conditions under which they can be applied. This advantage renders redox and light stimulus more desirable for certain applications, especially in comparison with thermal or chemical means.

Aside from tailored control of individual molecules, redox- and light- responsive units have also been integrated in bulk systems. For example, Zhu and coworkers developed a redox- and light-responsive organogel based on a new gelator **13** featuring electroactive tetrathiafulvalene (TTF) and photo-responsive azobenzene units (**Figure 15**).^[127] TTF is a popular class of redox-responsive units for its ability to switch to a stable radical cation state (TTF^{•+}) and a dication state (TTF²⁺) reversibly with chemical and/or electrochemical stimuli. Coupled with the azobenzene units, the conformation of the gelator and subsequently the intermolecular interactions can be altered. As shown in **Figure 15**, gelator **13** gels an organic solution of dichloromethane/methanol dissolved with an electrolyte, Bu₄NPF₆, to allow for subsequent electrochemical stimulation. When an oxidation potential was

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applied to the above gel, it converted to dark green solution after 90 s. The dark green solution was able to revert to the initial gel state with application of a small reduction potential for 140 s and subsequently heated and cooled. This electrochemically induced gel-sol transition was repeated for three cycles. The organogels also showed light-responsive properties. When **13** was dissolved in a similar dichloromethane/methanol solution without electrolyte, a comparable orange gel was obtained. Exposure to UV light (360 nm) at room temperature for 1 h resulted in gel-sol transformation, now without any visible color change. This solution could then be exposed to visible light ($\lambda > 460$ nm) for 2 h and cooled in the dark for 18 h, regenerating the original organogel. This transformation was again repeated for three cycles. This example of a sol-gel transition induced both by redox- and light stimulus demonstrates how the same principles used for operation of single molecular switches can be used to guide the design of bulk materials with complex functionalities.

Scherman and coworkers realized a route to reversible and tunable supramolecular 'grafting to' of polymer brush on a gold surface. Surface-bound CB[8] rotaxanes interacted via a host-guest recognition with both naphthol-terminated polyethylene glycol **14** and azobenzene-terminated polyethylene glycol **15**. When both functionalized polymers are present, the brush composition and density can be switched reversibly and efficiently using redox and light stimuli (**Figure 16**).^[128] The redox mechanism is driven by the methyl viologen (MV) unit tethering the rotaxane which can be reduced from MV^{2+} to MV^{+} , which breaks or blocks the heteroternary complex with **14** (**Figure 16A**). The light mechanism operates off the polymers themselves, instead of the substrate, by isomerizing

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the azobenzene unit to its *cis* form which would similarly affect the complex formation with **15** (**Figure 16B**). These two responses could be strategically manipulated by electrochemical and light stimulus to effectively pattern gold substrates with polymer brush (**Figure 16A**). Both processes are reversible, thereby demonstrating a patternable and re-writeable system. Huskens and coworkers also reported a photo- and redox- responsive supramolecular nanoparticles system.^[129] Their system contains cucurbit[8]uril (CB[8]), azobenzene-functionalized guest molecules, and the redox responsive unit methyl viologen (MV). These approach highlights a unique way to spatial control of supermolecular systems which moves us one step closer to the design of a universal platform for *in situ* surface engineering and drug delivery.

Given that photons and electrons are readily available, industrially used on scale and require minimal physical perturbation, the design and development of novel ways to integrate these privileged stimuli into complex materials will have a significant and immediate impact on the field. One area that is underexplored is leveraging the synergistic properties of photons or electrons to create high energy complexes that can lead to the development of novel transformations. Here, it will be important to understand how to design molecules that can be excited by photons and electrons and be long lived enough such that the active complex can be further excited using the complementary stimuli to generate a new catalytic species. This should enable the formation of highly reducing or oxidizing complexes, for example.

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7. Multi-photo- addressable architectures

Multi-photo- addressable architectures have long been highly desirable systems in various areas including signal transmission,^[130] biological manipulation,^[131] fluorescent materials,^[132,133] molecular switches, and logic gates.^[134] Compared with other multi-addressable architectures, they feature several advantages stemming from light being their only stimulus: (i) simultaneous and orthogonal stimuli can be applied very rapidly; (ii) no buildup of chemical waste and/or dilution; (iii) no requirement for addition of chemicals, wires, or other physical components; (iv) spatial and temporal control; and (v) remote controllability. To date, photochromic molecules have been integrated with many light-responsive components, including: other photochromic molecules, dendrimers, photosensitizers, fluorophores, and nanoparticles. These multi-photo- addressable architectures are extremely appealing platforms not only for the diversity of available candidates and their respective property changes, but also for the complex functions resulting from their mutual interactions.

The ability to selectively address photoswitches at different wavelengths in an orthogonal manner is highly desirable for these multi-photo- architectures, but still poses many challenges.^[135,136] When multiple identical photochromic units are totally isolated or separated by non-conjugated spacers, each unit behaves independently so that the light-responsive behavior happens as a combination of all the individual units. Conversely, if multiple identical units are connected by electronically coupled (namely, π -conjugated) organic spacers, the light-induced transformation of a single unit will affect the photoisomerization of the adjacent units due to unavoidable intramolecular excited state energy

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transfer.^[137] In both case, stepwise and selective photoisomerization cannot be performed. To address the above problem, the strategy of combining different photochromic molecules that feature distinct photoswitching properties has been developed in several labs, namely the Feringa group and our group. In these systems, photochromic molecules are electronically decoupled from each other to minimize energy transfer between chromophores, thus retaining independent switching selectivity. Feringa and coworkers investigated an intermolecular combination of two different types of photochromic molecules as well as their intramolecular analog to highlight this phenomenon in orthogonally photo-addressable molecular systems.^[84] As shown in **Figure 17**, the photoswitches used in this study consisted of an azobenzene (**16**) and a DASA (**17**). The intermolecular combination of photoswitches **16** and **17** showed impressive wavelength selectivity, as indicated by the photochromism plots (**Figure 17A**). Selective and nearly quantitative *trans-cis* isomerization of **17** can be achieved with 370 nm light irradiation. Irradiation of the resulting *cis* isomer (at 430 nm) led to *cis-trans* transformation, all while having no observable effect on **16**. Similarly, **16** could undergo cyclization selectively by 590 nm light irradiation without affecting **17** and would then relax back to its thermally stable state with a short thermal half-life of 37 seconds at room temperature. Selective switching of **16** was also achieved by 590 nm irradiation when **17** was in its *cis* form (via 370 nm irradiation). This ability to orthogonally switch either of the two photochromic molecules in an intermolecular combination was successfully demonstrated across a large concentration range. The selectivity in an intramolecular combination was also investigated in this work by synthesizing intramolecular analogs with both azobenzene and DASA units connected

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by alkyl linkers of different lengths. Although the selective switching of the azobenzene unit was retained, irradiation with 590 nm could not selectively switch the DASA unit without also affecting the azobenzene. Similarly, a wavelength selective intermolecular switching system based on different generations of DASAs was designed in our group.^[80] As shown in **Figure 17B**, DASAs **18** and **19** were chosen due to their minimal overlap in absorption, with a absorption maxima at 560 nm and 623 nm, respectively, in toluene. When the mixture of **18** and **19** in toluene was irradiated with higher than 650 nm light, DASA **18** was selectively isomerized from open to closed form. The color of the solution changed from an initial indigo to bright pink. When the mixture was irradiated by 514 nm high-bandpass-filtered light, DASA **19** was selectively switched with minimal isomerization of **18**, changing the solution from indigo to turquoise. The selective and reversible switching of mixtures of DASA derivatives has also been demonstrated in solid state.^[138] Building on this work, Bruns, Boesel, and Read de Alaniz reported a light-responsive DASA-containing polymersome nanoreactors to realize wavelength-selective changes in the permeability of the polymersome membranes.^[139] These examples represents a major step towards the development of future orthogonal and reversible photo-switchable systems that can be used for non-invasively modulating multiple functions within a system. Because of the remote and benign nature of light as a stimulus, these types of systems are of great interest in the areas of microfluidics and drug delivery. However, especially in drug delivery, the fact that these photoswitches require UV and visible light irradiation is very limiting. Because tissue absorbs strongly in the UV and visible regions, extending the absorption of photoswitches to the infrared would be hugely impactful for biomedical applications. Increasing the working range of

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wavelengths for photoswitches would simultaneously help to address the issue of selective stimulation.

Controlled actuation of soft matter using light is an emerging area in materials science. One promising strategy involves generating liquid-crystalline networks incorporating photoswitches that undergo photoisomerization. In 2009, Broer and coworkers fabricated micro-actuators with different azobenzene subunits, one with a peak absorption in the UV (360 nm) and the other in the visible (440 nm). To generate their materials, a resin containing the photoswitches and liquid crystals was printed by inkjet and photopolymerized. These devices, designed to mimic the movement of natural cilia, were printed as a variety of flaps such that irradiation of different wavelengths of light selectively promoted two modes of bending.^[140] Similar work in soft actuation by liquid crystal and photoswitch containing networks was done by Broer's group in 2017.^[51] The photoswitch is an azomerocyanine (**20-AM**) dye with pH-responsiveness. When treated locally with acid, it switches to the hydroxyazopyridinium form (**20-HAP**) allowing for spatial resolution of patterning (**Figure 18**).^[51] The two forms of the dye have different enough absorptions to provide a window for programmable actuation, and so the ability to selectively isomerize the two forms was studied with 405 and 530 nm light. To observe the dual-response, a AM-containing polymer film was kept stationary at one end while light was exposed to the other end. The splay aligned film showed significant bending (reaching 50°) with 530 nm light irradiation and to a lesser extent (20°) with 405 nm light irradiation (both at 185 mW cm⁻²). For the acid-treated film (now in the HAP form), inverse bending behavior

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was observed under the same irradiation conditions: with 530 nm light irradiation the film showed minor bending (10°), but with 405 nm light the bending was significant (50°). Interestingly, due to their rapid thermal recovery, the films immediately recovered their initial conformation upon removal of the light stimulus. Despite the impressive results, this system could not demonstrate completely orthogonal light response due to the minor absorption overlap of the two forms. This example speaks to another challenge in achieving orthogonal control for multiple photoswitches: even with significantly different peak absorptions, the width of these peaks can lead to significant overlap and loss of control.

In addition to the photochemical mechanism (usually photoisomerization of azobenzene molecules), the light-induced deformation of liquid-crystalline networks can also go by a photothermal mechanism. Photothermal actuation involves converting light energy into heat, such that the generated heat can induce: a change of phase, an expansion in volume, release of molecules, or surface tension effects. For example, our group demonstrated waveguiding photo-actuators based on hydrogels nanocomposites with photothermally addressable components.^[141] The photo-actuators are comprised of gold nanoparticles incorporated into thermally sensitive PNIPAM hydrogels and exhibited fast and reversible bending behavior with visible light irradiation. With strategic placement of the embedded nanoparticles, the hydrogels can be designed to promote different bending behaviors based on the direction of light as well. Recently, Priimagi and coworkers demonstrated reconfigurable actuation by combining photochemical and photothermal responses

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within a single liquid-crystalline network actuator. Using UV irradiation, the *cis*-azobenzene content can be modulated to program the response of the actuator, after which red light can be used to trigger the actuation via a photothermal effect. In this work, a single actuator was reversibly programmed with 6 different shape changes under the same irradiation conditions with the use of a photomask.^[142] Often in discussion of photoswitches, photothermal effects are neglected or minimized, but here are demonstrations that the effect can be synergistically harnessed for the generation of materials with complex behaviors.

In addition to the above liquid-crystalline network materials, Asanuma and coworkers designed a DNA nanomachine that exhibited a seesaw-like motion driven by light of different wavelengths.^[136] The working principle of this nanodevice is that only in the planar *trans*-conformation do the azobenzenes stabilize the duplex via stacking interactions. In their work, 2,6-dimethyl-4-(methylthio) azobenzene-4'-carboxylic acid (**21**) and azobenzene-4'-carboxylic acid (**22**) were chosen for their different absorption properties. The DNA nanodevice used four different oligonucleotides: an "L bar" containing five residues of **21**, an unmodified "M bar", an "R bar" containing five residues of **22**, and a "Temp" (template) component as shown in **Figure 19a**. The response of this nanodevice under different light irradiation is illustrated in **Figure 19b**. First, when the nanodevice was irradiated with 450 nm light, *cis-trans* isomerization happens for both **21** and **22**, leading to the formation of L bar/Temp and the R bar/Temp duplexes (state a). Upon irradiation of the device at 390 nm, *trans-cis* transformation only happens for **21** with no influence on **22**, resulting in the dissociation of L

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bar/Temp duplex while the R bar/Temp duplex remains unaffected (state b). Interestingly, 340 nm light induces the *cis-trans* isomerization of **21** and the *trans-cis* isomerization of **22**, resulting in state c with a stable L bar/Temp duplex and a dissociated R bar/Temp duplex. Finally, both **21** and **22** undergo *trans-cis* transformation with 370 nm light irradiation, so that the L bar/Temp and R bar/Temp duplexes are both unstable (state d). In this example, careful selection of photoswitches enabled the generation of a DNA nanodevice that can transform between four distinct states by irradiation of four different wavelengths of light. In realizing this system, the researchers exploited the overlap of the azobenzenes, with careful attention to the overlap of their *cis/trans* conformations, to selectively isomerize either one of or both units independently.

While orthogonally switchable photo- and photonic- addressable architectures are generally more desirable, in a well-designed light-responsive system there can be benefits to controlled crosstalk in numerous applications. Of particular interest, photochromic compounds coupled with fluorophores have led to fascinating systems with reversible fluorescence intensity modulation.^[143–147] The functionality in such systems relies on controlling an energy transfer process by interconverting between the on and off states of a photoswitch. Diarylethenes (DAE) are promising candidates for this application because of the huge shifts in absorption (usually from 250–330 nm to > 500 nm) that accompanies their photocyclization, as well as their thermal stability and fatigue resistance. Furthermore, DAE tend to act efficiently as energy acceptors during energy transfer processes, with the nature of the energy transfer differing largely based on the photo-state. Since Jares-Erijman and

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coworkers first reported in 2002 their fluorescence on/off photoswitching system based on a fluorescence resonance energy transfer (FRET) mechanism using a diheteroarylethene as acceptor, lots of work concerning fluorescence modulation of DAE-based photo-addressable fluorophores has emerged. To date, DAE has been integrated with boron-dipyrromethene, π -conjugated small molecules, porphyrin, lanthanide complexes, and nanoparticles.^[144,145,147–149] In one example, Park and coworkers illustrated chameleon nanoparticles and polymer films with tunable fluorescence based on a multicomponent system by taking advantage of FRET in the presence of a photochrome.^[148] There are three components in the systems: photochromic compound **25**, and fluorescent organic materials **23** and **24** (**Figure 20A**). Colloidal nanoparticles containing the above three species were synthesized via reprecipitation. Compound **23** shows emission around 472 nm and can play the role as donor for both **24** and the closed-form **25**, but not the open-form **25**. The closed-form **25** is a nonradiative acceptor for both **23** and **24**. Initially, the emission color of the three-component nanoparticles was pink-red (due to partial FRET from **23** to **24**). However, when **25** is ring-closed with UV light, the emission changes to blue, as the shifted absorption of **25** overlaps more efficiently with the emission of **24** (**Figure 20B**). This tunable fluorescence color change was attributed to fluorescence-color-selective quenching dictated by the photoswitch. The emission could be returned to its original color by returning **25** to its open-form via irradiation of visible light ($\lambda_{\text{irr}} > 550 \text{ nm}$), demonstrating a completely reversible system. To further demonstrate their utility, the nanoparticles were incorporated into a PMMA film and were shown to retain their switching character (**Figure 20C**). This system illustrated a noninvasive readout of the fluorescence signal and

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can be used for fluorescent optical memory. Besides fluorescence modulation, other applications of diarylethene-based photo-addressable architectures with energy transfer processes (e.g. photochemical control of singlet oxygen generation) have also been recently demonstrated.

Photons as the multi-addressable energy source offer many enabling advantages that are only recently starting to be realized now that photoswitching molecules with wavelength tunability have been developed. Certainly, the incorporation of UV and visible light active photoswitches into polymeric material will be of increased interest as this approach holds tremendous promise and leverages existing systems. However, this area will greatly benefit from the design and development of novel photoswitches with wavelength tunability to further expand the tool box available for multi-addressable photo-based systems.

8. Photo- with other stimuli- addressable architectures

In addition to the above multi-addressable architectures, coupling photo- with chemical-, thermal-, redox-, or photo- addressability, photoswitches have been uniquely integrated with various other stimuli-addressable units that do not fit in the aforementioned categories. For example, Park and coworkers reported a novel low-power soft actuator based on their light- and electro- sensitive polymer (LEAP).^[17] This actuator is made by the layering of two distinct materials: an electro-active polymer (EAP) of sulfonated triblock copolymer doped with imidazolium salts ionic liquid; and a

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light-active polymer (LAP) from a mixture of azobenzene-containing salts and a random copolymer containing charged ammonium chloride units. For the EAP layer, ion migration occurs with application of voltage; for the LAP layer, *trans-cis* isomerization occurs with light irradiation. Both layers were found to be independently responsive, with rapid bending of the LEAP actuator observed under electro- and/or light stimuli. Furthermore, the actuator can “lock” itself in a photo-induced conformation, maintaining the deformation for tens of minutes even after removal of light. This behavior is caused by the slow isomerization from *cis* to *trans* of the azobenzene unit and the large blocking force created by the stiff LAP layer. In another work featuring a less common stimulus, photoswitches coupled with ligand field-responsive metal centers was developed by Frank and coworkers. The photoswitch, a spirooxazine-cobalt-dioxolene complex, can convert between two forms with distinct ligand fields thereby dictating the oxidation and spin state of a bound metal center even in the solid state. Previously, opto-spintronic devices that operated off photomagnetic metal centers were limited to low temperatures because above cryogenic temperatures the excited states relax on the order of nanoseconds. This demonstration of using a spiropyran-based photoswitch to modulate between two bistable optically gated spin/charge states is impressive in that it demonstrates a novel route to a photomagnetic spintronic system that performs at device conditions (300–330K) and with lifetimes on the order of 10 seconds.^[150]

Interestingly, spiropyran (SP) is not only a thermochromic and photochromic molecule, but also a color-changing mechanophore.^[151–153] When strain is applied across SP molecules, it can reduce the

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barrier for cleavage of the weak C–O spiro bond leading to conversion to the merocyanine (MC) form. Thus, SP provides lots of opportunities for multi-stimuli architectures by exploiting their photo-, thermo-, and mechano- responsivities together. For example, a thermo-, photo-, and mechano-responsive poly(acrylamide-co-methyl acrylate)/spiropyran hydrogel has been developed by Zheng and coworkers.^[154] These hydrogels exhibited remarkable optical responsiveness in their ability to switch between two highly colored states (yellow and red), accompanied by a switch in fluorescence from green to red. Switching from the initial SP yellow state to the red MC form was achieved by UV irradiation, heat, and mechanical force. In all cases, the original SP form could be recovered with visible light irradiation. It was found that the mechanical force was absorbed by ring-opening of the SP unit, resulting in a dramatic toughening of the hydrogels. The photoswitch enables high recovery of the strength of the material by simple irradiation, demonstrating a reversible mechanophore-toughening hydrogel.

These examples illustrate that photoswitches can be integrated into systems with a broad range of stimuli-responsive systems to create a variety of high performing materials with complex behavior. Because of the versatility and expansive range of photoswitches being added to the toolbox these materials have a wide range of possibilities, with applications limited largely by the imagination. However, it will remain critical that there is a focus on understanding the photophysical properties of existing and new photoswitching molecules to enable chemists, material scientist and engineers to construct complex systems that work reliably and under almost any conditions.

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9. Conclusion

Clearly, incorporation of light-responsive photochromic molecules with various other stimuli-responsive components is an efficient strategy for developing functional smart materials. (i) This strategy enables the design and fabrication of sophisticated systems with more complex functions and better performance when compared to single stimuli-addressable systems. For example, by rational design of structures and manipulation of interplay between components, complex molecular logic systems, such as keypad locks,^[155] parity generators/checkers,^[156] and multi-state switches based on multi-addressable photochromic architectures have been achieved. These molecular logics realize the functions of information protection, error detection etc., and pave the way for future molecular computing. (ii) This strategy provides a platform for 'on-demand' control over the behaviors of different functional systems. By incorporating photochromic molecules with other functional systems, the independent spatiotemporal regulation can impart dynamic control over material properties, as demonstrated with the formation of a hydrogel, orthogonal drive of the motion of a DNA switch, and control over the kinetic rates of a molecular shuttle. (iii) These photochromic based multi-component systems represent a large advancement towards cleaner and more efficient chemical systems. As shown, photoacids can help mitigate waste generation during chemical processes. In addition, "clean fuel" photons and electrons are widely exploited as triggers

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to operate multi-components systems, similarly generating no waste nor leading to chemical accumulation.

While lots of exciting progress has been made, there are still some key challenges to be addressed. From a molecular design perspective, 1) photoacids with increased photo-acidities, improved solubility in solvents with different polarity, controllable reverse reaction rate, low dark acidities and high quantum yields is highly desirable to fulfill the demand of various applications. 2) Only P-type photoswitches can be used for design of photo- and thermal- addressable architectures. However, relatively little insights into the “design rules” for P-type photoswitches are developed. 3) Operation at solid state is favorable for applications such as light-responsive actuator and electronic junctions. Compared with solution states, the photoswitching efficiency at solid state is relatively low and design of photoswitches featuring improved efficiency in solid state is highly favorable. 4) The most commonly employed photochromic molecules, such as azobenzenes, diarylethenes, and spiropyrans, have overlapping absorption bands in the UV-Vis region, and typically isomerize with UV light irradiation. Attempts to realize logic control with these photoswitches in a single system (e.g. orthogonal switching) becomes difficult due to their similar photoswitching properties. Thus, development of new photochromic systems with absorption ranges distinct from these privileged classes is important for advancement of multi-addressable systems. In addition, although great strides have been made to improve the properties of existing photoswitch systems, such as stability and quantum yields, there is still substantial room for improvement. 5) In areas like

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photopharmacology, development of light-responsive molecular tools which are triggered by visible or near-IR light and feature good water solubility, low toxicity, metabolic stability, and thermal stability of the isomers, are still highly desired.^[37] 6) The effects of external stimuli, such as load, current, and stress, on the photophysical properties of photoswitches needs to be better understood as we transition from photoswitches operating in isolation to more complex systems that require multi-stimuli.

The ongoing interest in molecular devices and machines is derived not only from their fundamental importance, but also their demonstrated potential in applications such as nanomedicine, multi-analyte detection, and smart materials. Thus, moving these functional systems from solution to surface, polymers, or biological environments is vital to realizing their potential in future technologies. For these purposes, 1) effective methods to link different kinds of photoswitches to surface, polymers, and biological substrates are highly desirable. In most cases, covalent bonding is preferred as it can avoid problems with leeching, solubility and greatly improve the compatibility between photoswitches and the target substrate. 2) Although multi-stimuli systems have good performance, architectures with more precisely controllable behaviors are still under investigation, such as actuators with controllable bending speed and quantitative deformation stress. Development of analytic methods and models correlating the macroscopic changes in properties to molecular-level structural change is important for deepening the understanding of these systems and aiding the development of systems with more sophisticated functions. 3) In some cases, light

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penetration needs to be taken into consideration, especially for systems that rely on ultraviolet light which is known to have poor penetration in most solid materials. Although efforts are still needed to address these concerns, recent exciting achievements in photoswitch-integrated systems strongly suggest that this is a critical research space for the development of future technologies and advanced materials.

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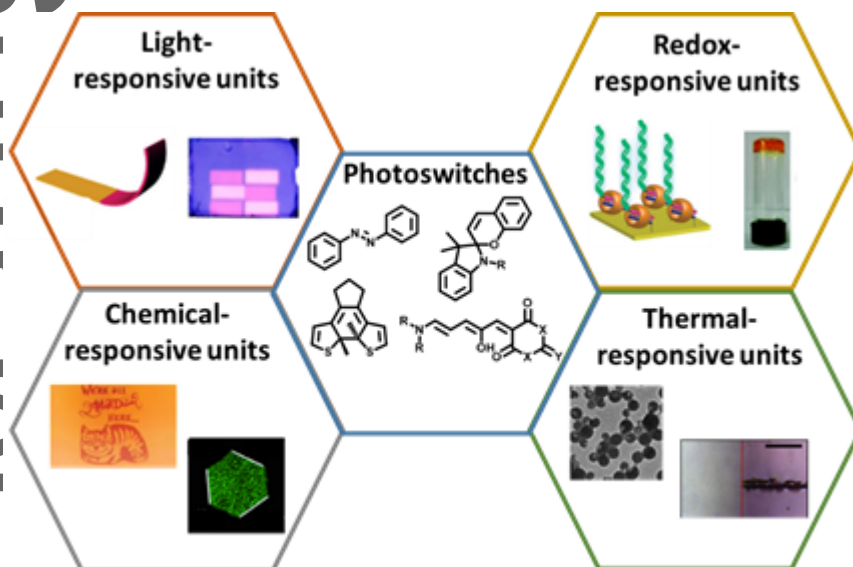
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Scheme 1. Multi-addressable photochromic architectures and their applications. Top left: Reproduced with permission.^[138] Copyright 2017, American Chemical Society (ACS). Reproduced with permission.^[51] Copyright 2017, Wiley-VCH. Top right: Reproduced with permission.^[127] Copyright

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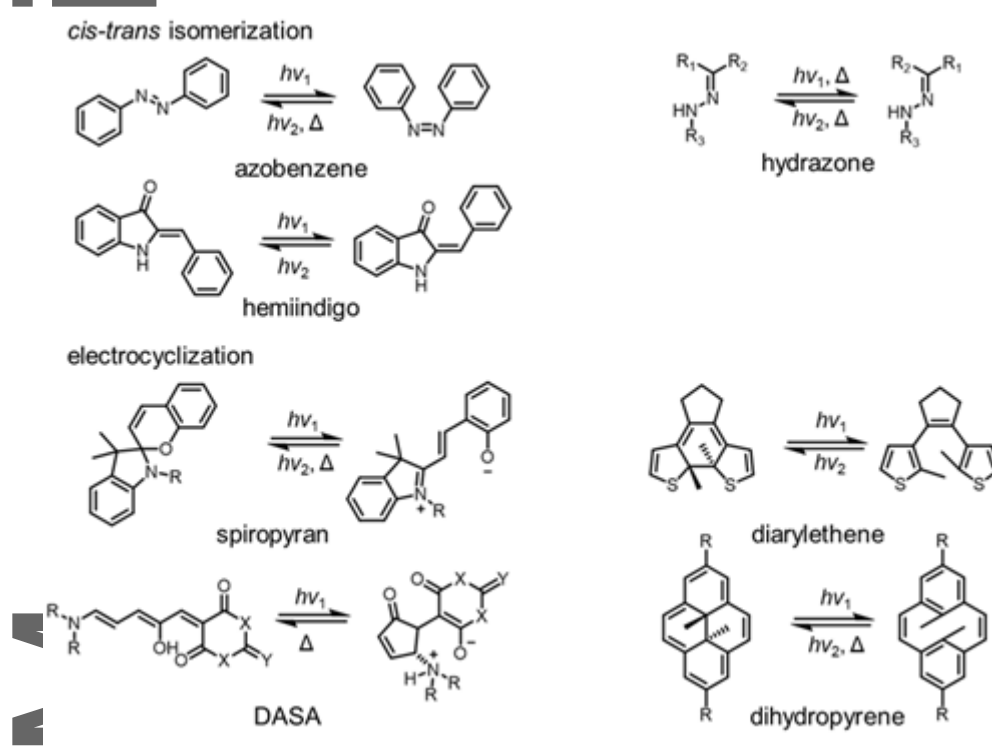


Figure 1. Select photoswitch structures and corresponding photoisomerization.

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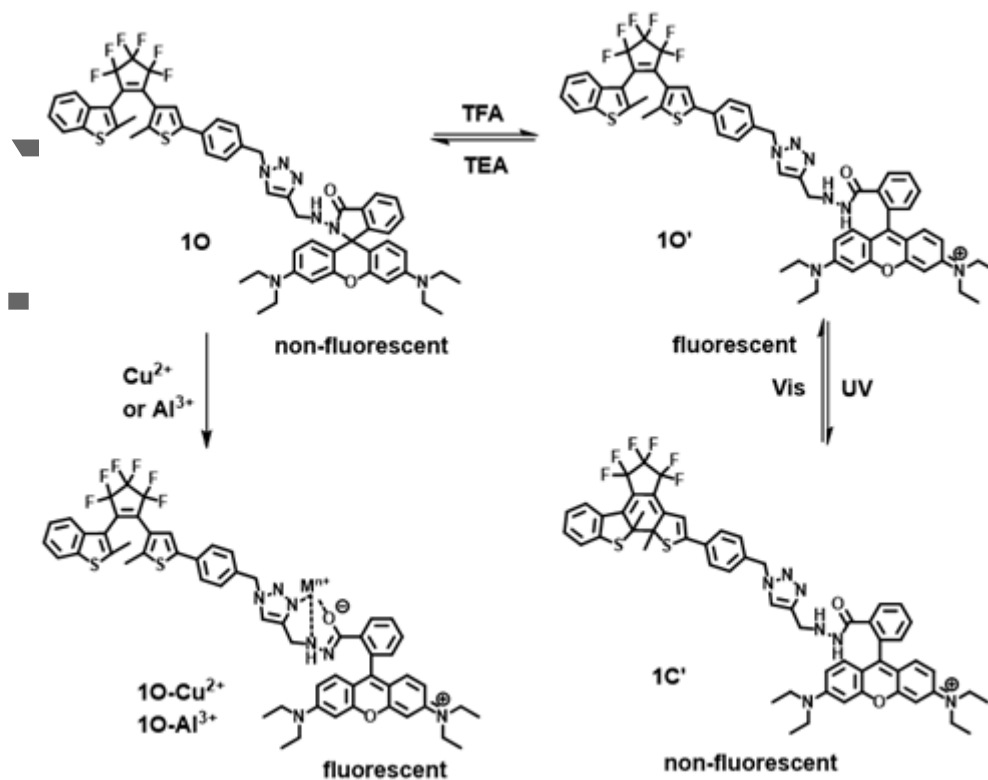


Figure 2. Principle of fluorescence switching for compound **10** stimulated by proton or metal ions or light. This logic circuit uses light and chemical species as inputs and the fluorescence intensity at 595 nm as output. Reproduced with permission.^[93] Copyright 2014, American Chemical Society (ACS).

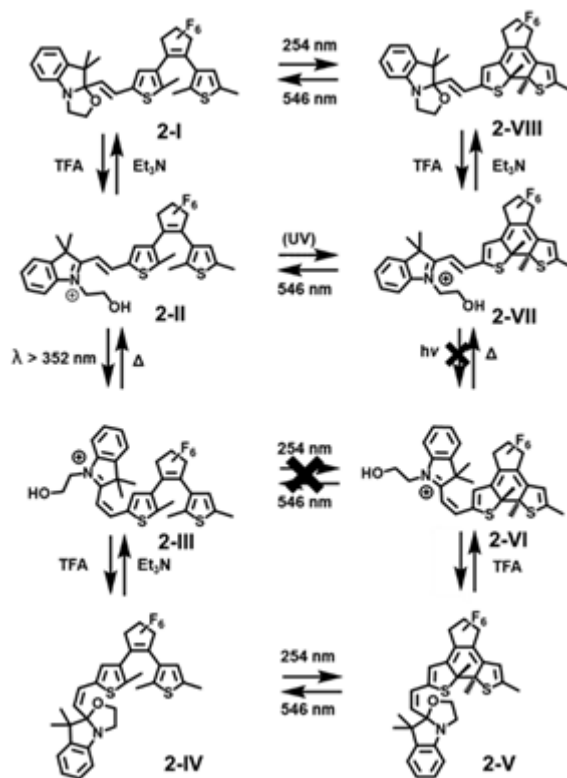


Figure 3. Modulability of the octa-state switch **2** featuring electrocyclization of dithienylethene, Z/E isomerization and acid–base oxazolidine change. Reproduced with permission.^[94] Copyright 2014, American Chemical Society (ACS).

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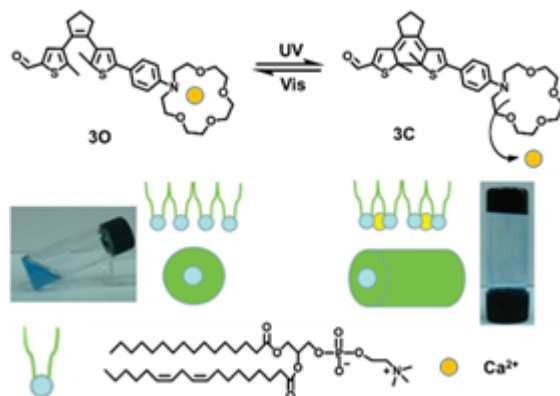
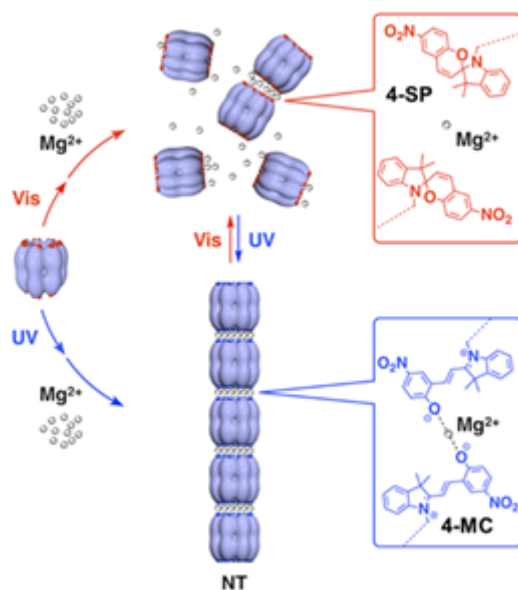


Figure 4. Photo-controllable gel-to-sol transformations of two-component lecithin- Ca^{2+} gels. The bis-thienylethene with aza-15-crown-5-ether groups **3** could reversibly capture and release calcium ions with light irradiation. Reproduced with permission.^[95] Copyright 2013, Royal Society of Chemistry (RSC).



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Figure 5. Schematic illustrations of light-mediated formation/dissociation of SP modified protein nanotubular assembly via the controlled generation of $MC \cdots Mg^{2+} \cdots MC$ bridges. Reproduced with permission.^[96] Copyright 2013, American Chemical Society (ACS).

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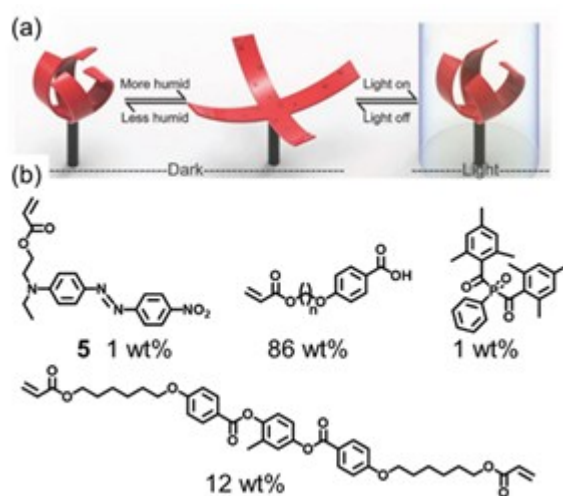


Figure 6. Realization of an artificial nocturnal flower. (a) Schematic representation of the nocturnal actuator: the flower opens at high humidity level in absence of light and closes in the presence of light or when the humidity is low. (b) Composition of the LC mixture used in fabrication of the nocturnal actuator. Reproduced with permission.^[36] Copyright 2019, Wiley-VCH.



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Figure 7. Efficient multistep switching process of triethylene glycol monomethyl ether functionalized hydrazone switch with light irradiation of MC derivative. Reproduced with permission.^[106] Copyright 2014, American Chemical Society (ACS).

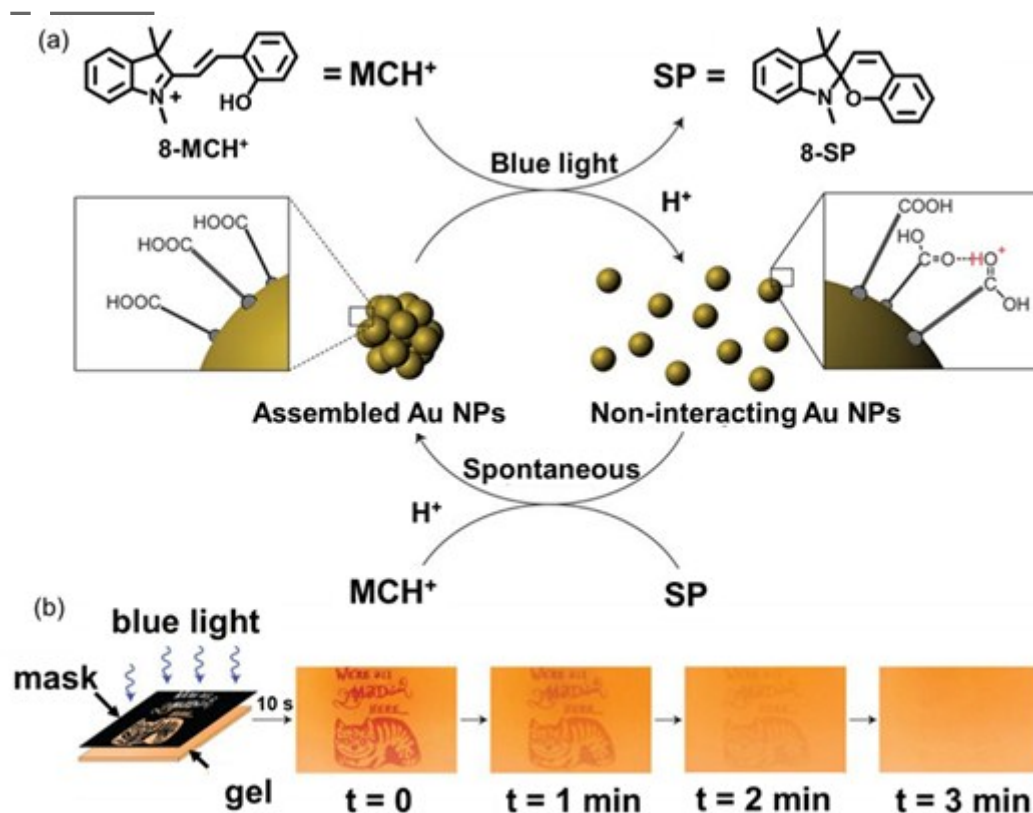


Figure 8. (a) Light-controlled self-assembly of NPs functionalized with ligands terminated with COOH groups. The self-assembly of NPs happens in a photo-switchable medium containing 8-MCH⁺. When 8-MCH⁺ is exposed to blue light, the acidity of the medium increases, which consequently induces the disassembly of NPs connecting by hydrogen bonds. Reassembly of the particles occurs spontaneously in dark or under ambient conditions. (b) Self-erasing images in a photo-responsive gel

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by light-controlled self-assembly of non-photo-responsive NPs. Reproduced with permission.^[75] Copyright 2015, Nature Publishing Group.

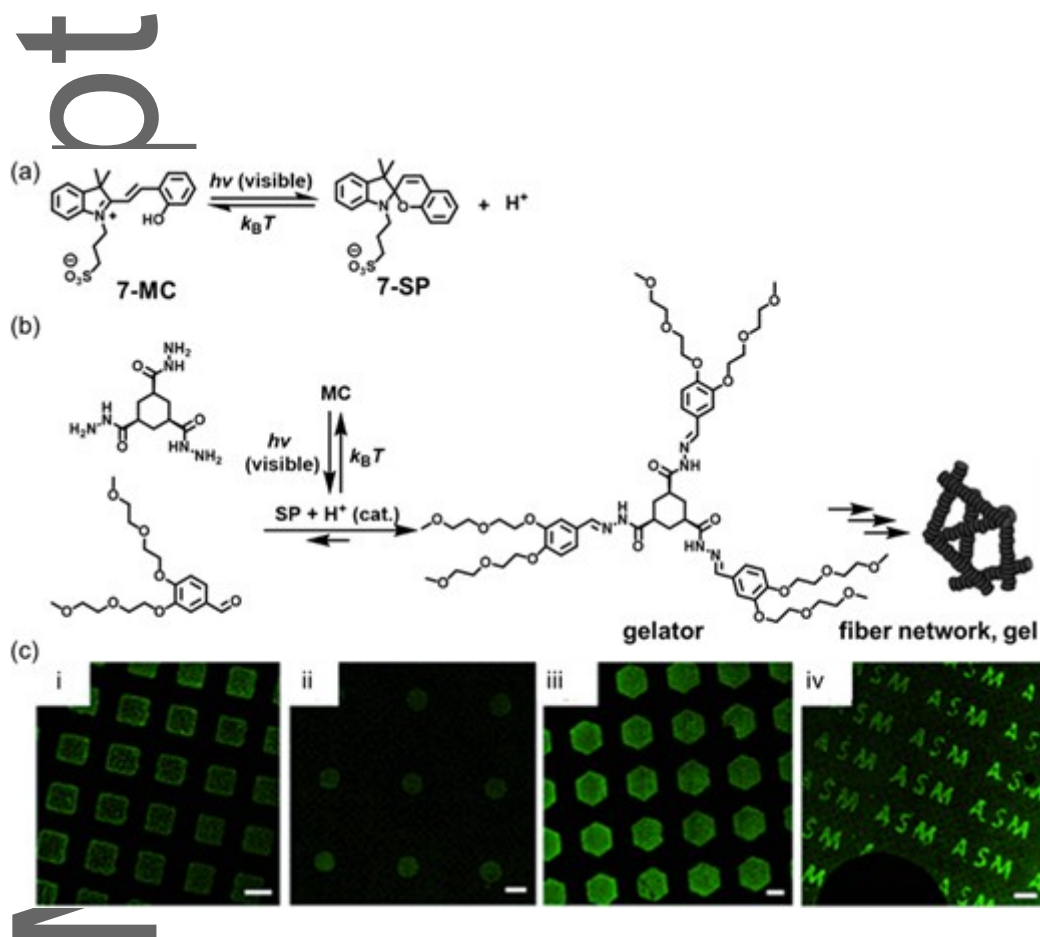


Figure 9. Supramolecular gelation using photo-switchable catalyst **7**. (a) Visible light irradiation of the catalyst drives the conversion of **7-MC** to **7-SP** form with generation of a proton. Thermally activated conversion back to **7-MC** removes the proton from solution. (b) Trishydrazone gelator formed from trishydrazide and benzaldehyde with photo-switchable catalyst leads to gelation through the generation of a crosslinked fiber network. (c) Gel patterning by light: (i-iv) CLSM of gel patterns formed with irradiation through the mask. Scale bar: 500 nm. Reproduced with permission.^[104] Copyright 2015, Wiley-VCH.

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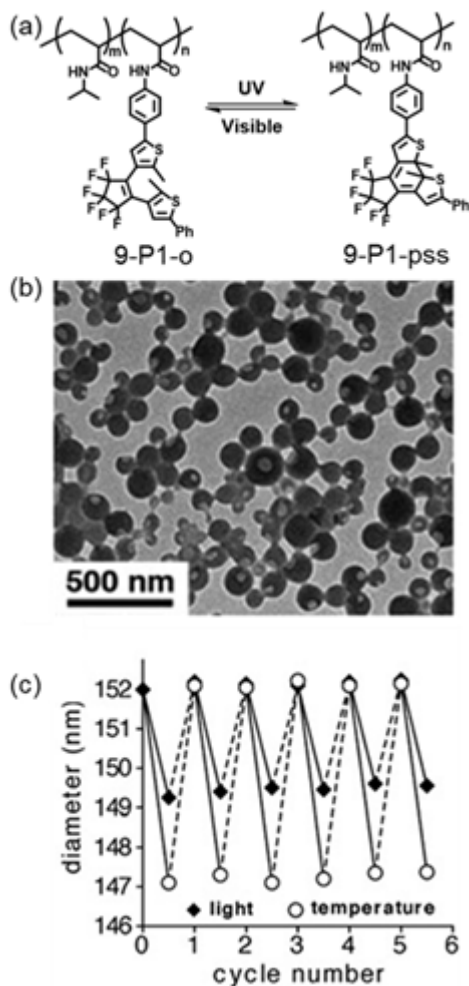


Figure 10 (a) Structures and photoswitching of copolymers **9-P1-o** and **9-P1-pss**; (b) Transmission electron microscope image of the copolymeric nanoparticles **9-P1-o** (DTE in its open form). (c) Reversible switching of average hydrodynamic diameters of **9-P1-o** nanoparticles with alternate exposure to UV light (313 nm, 5.5 mW cm⁻², 2 min; dashed line) and visible light (> 500 nm, 300 W, 5 min; solid line) at 20 °C and with alternating high (60 °C; solid line) and low (20 °C; dashed line)

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temperatures at the 313 nm photostationary state. Reproduced with permission.^[112] Copyright 2011, Elsevier.

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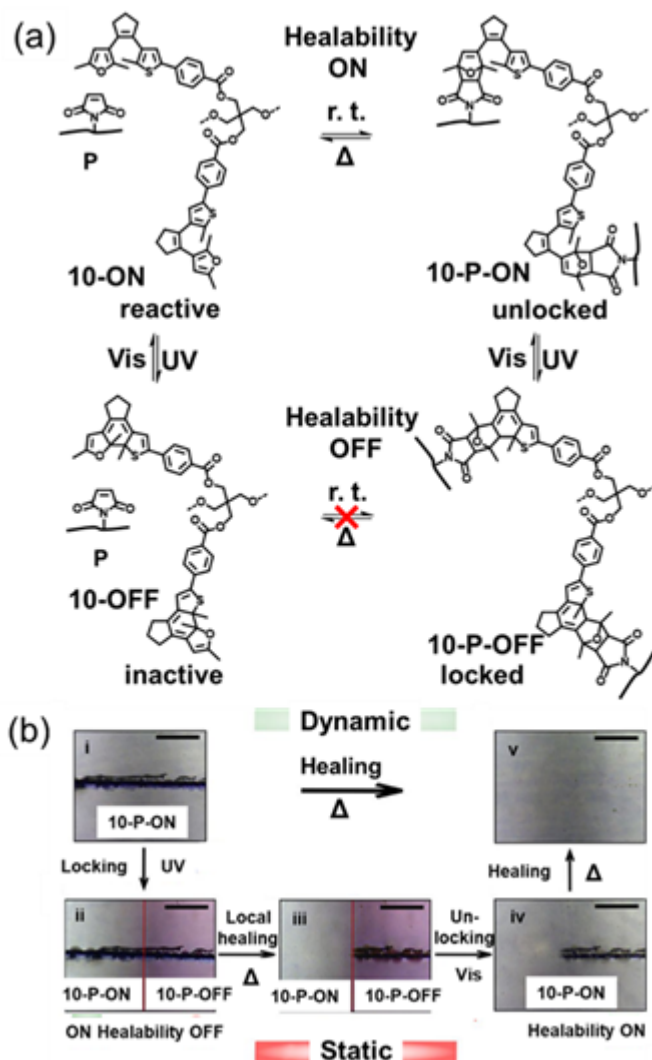


Figure 11. Light controllable thermal healing of dynamic polymer networks. (a) Chemical structures of the tetra-furyl-substituted diarylethene crosslinker **10-ON** and **10-OFF**, and their reactivity towards maleimide-functionalized poly(lauryl methacrylates) via a Diels–Alder reaction. (b) Light

controllable self-healing of a scratched thin film. Scale bar, 0.3 mm. Reproduced with permission.^[116]
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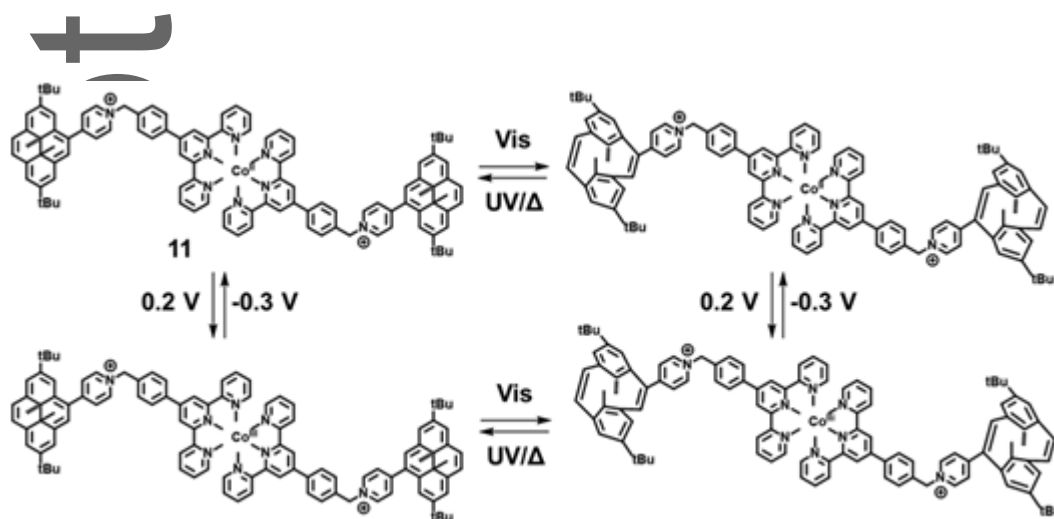
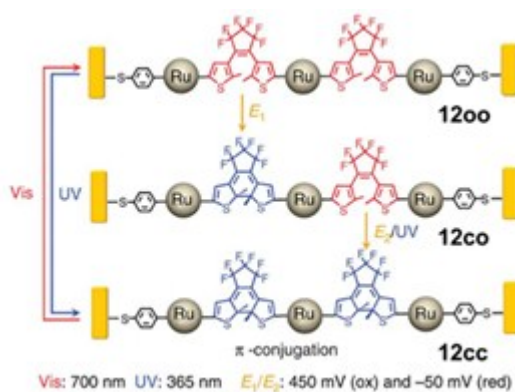


Figure 12. Multi-addressable states for the **11** $\text{Co}^{\text{II}}(\text{Lc})_2^{4+}$ complex modulated by photo- or thermal- and electrochemical redox- stimuli. Reproduced with permission.^[122] Copyright 2016, Royal Society of Chemistry (RSC).



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Figure 13. Trimetallic complex with two DTE units functionalized nanogap devices. Scheme of molecular isomerization of **12** under different external controls. E1 and E2, two cycles of electrolysis; Reproduced with permission.^[123] Copyright 2014, Nature Publishing Group.

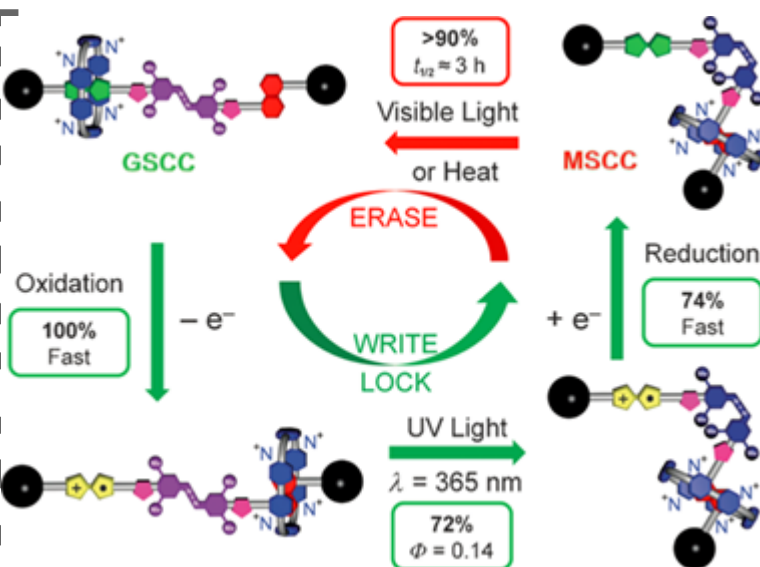


Figure 14. Photochemically and chemically triggered memory switching cycle of the [2]rotaxane. Oxidation stimulus wrote the data on the rotaxane. Data was locked by UV light irradiation. Subsequently reduction led to the formation of metastable state co-conformation (MSCC). The data can be erased by Vis light irradiation or heating. Reproduced with permission.^[126] Copyright 2012, Wiley-VCH.

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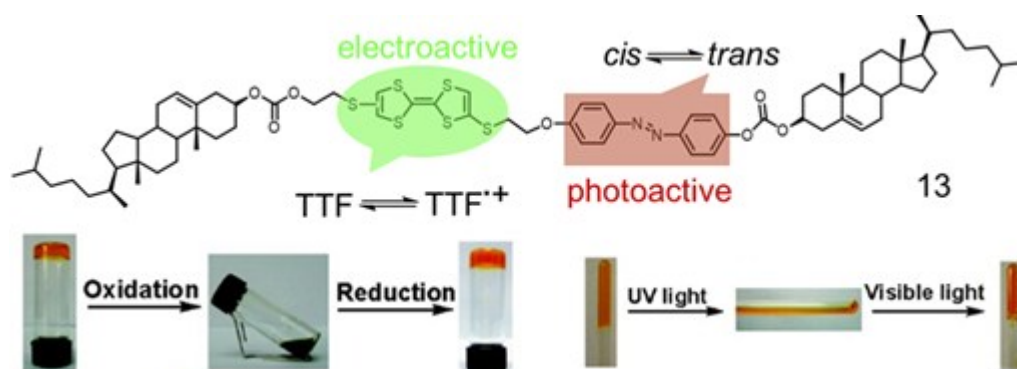


Figure 15. Chemical Structure of **13** and schematic representation of the design rationale for reversible multistimuli responsive organogels. Reversible tuning of the organogels formation (left) by redox stimuli and (right) by light irradiation. Reproduced with permission.^[127] Copyright 2010, ACS.

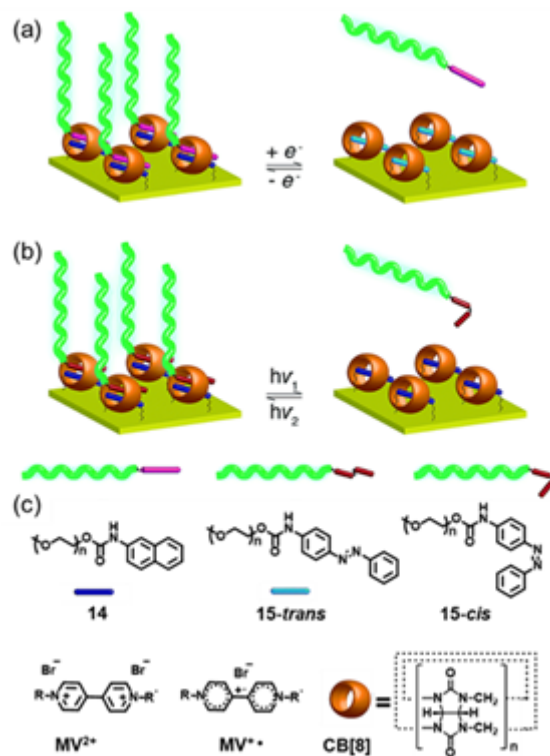


Figure 16. Schematic illustrations of CB[8]-mediated supramolecular ‘grafting to’ polymer brush preparation of (a) redox-driven assembly and disassembly of **14** and (b) photoisomerization-driven reversible assembly of **15**; (c) chemical structures of different components. Reproduced with permission.^[128] Copyright 2015, RSC.

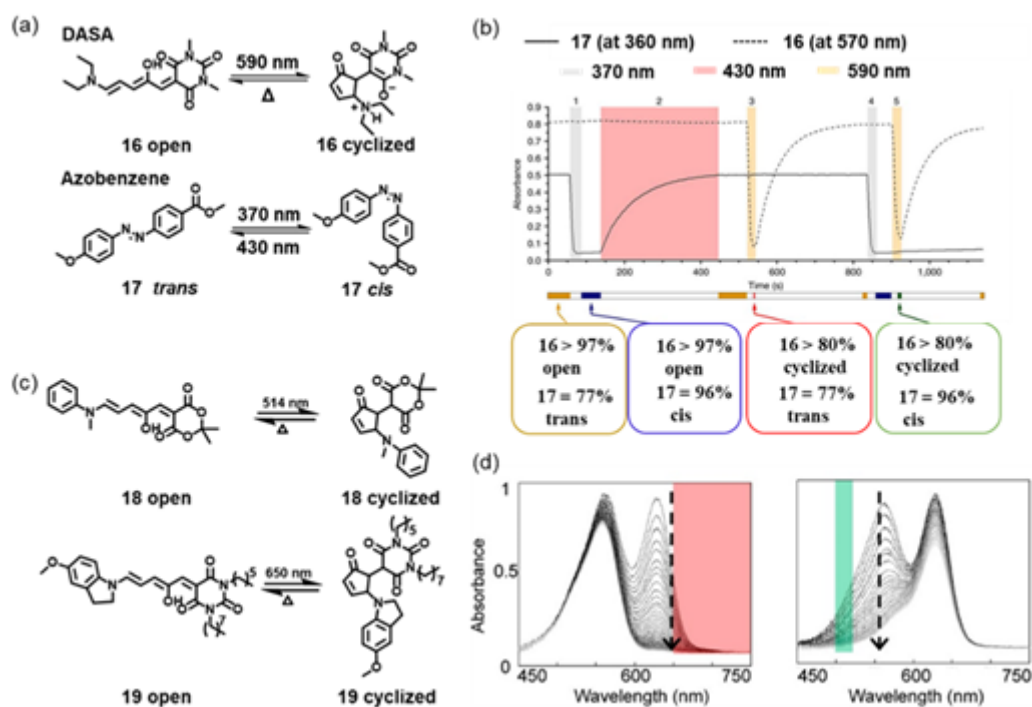


Figure 17. (a) Structures of DASA **16** and azobenzene **17** photoswitches. (b) The orthogonal photoswitching of both compounds in one solution was monitored at characteristic wavelengths for each photoswitch (360 nm for **17** and 570 nm for **16**). The structure of photoswitches and their corresponding photostationary states are given for the different states during photoswitching. Reproduced with permission.^[84] Copyright 2015, Nature Publishing Group. (c) Structures of DASA **18** and **19** photoswitches. (d) Selective photoswitching of two mixed DASAs (**18** and **19**) using filtered broadband white LED. Compounds **18** and **19** were mixed in toluene followed by photoswitching via irradiation through a 514 nm bandpass filter to cyclize **18** or a 650 nm long-pass filter to cyclize **19**. Reproduced with permission.^[80] Copyright 2016, ACS.

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Figure 18. (a) Molecular structure of **20-AM** and its changes upon acid and base treatment. (b) Schematic of the rewritable polymer actuator. The yellow regions contain **20-HAP** dye and the magenta regions contain **20-AM** dye. Reproduced with permission.^[51] Copyright 2017, Wiley-VCH.

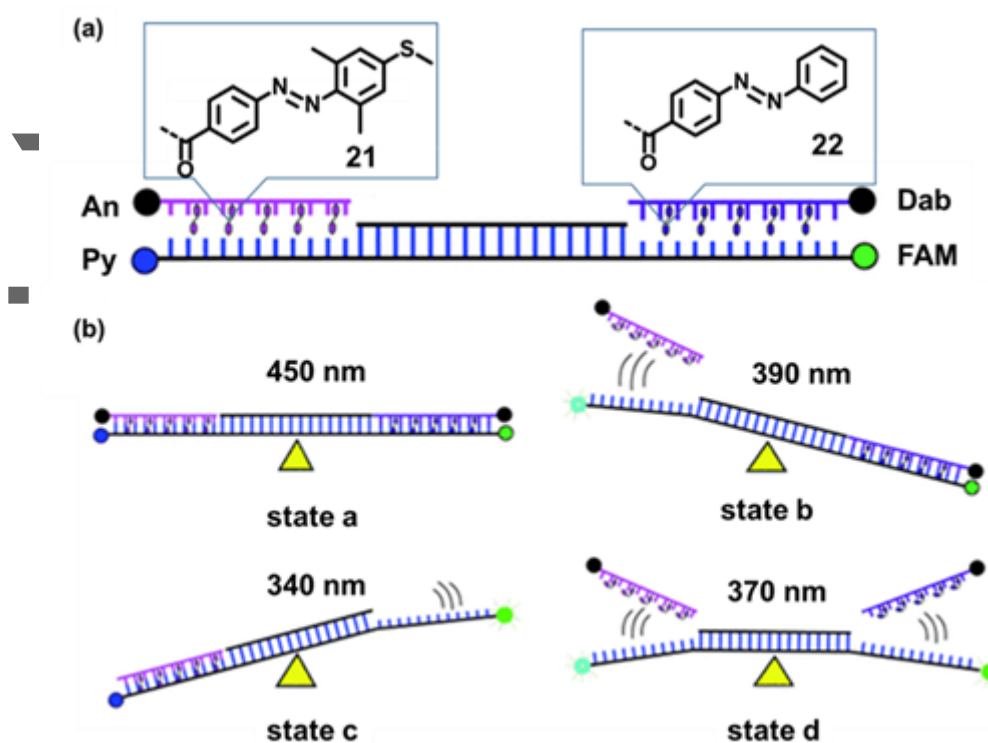


Figure 19. (a) Illustration of the design of a DNA nanodevice containing **21** and **22** modified DNAs. (b) Four possible states (a, b, c, and d) of the nanodevice are achieved by irradiation at four wavelengths (340 nm, 370 nm, 390 nm, and 450 nm, respectively). Reproduced with permission.^[136] Copyright 2012, Wiley-VCH.

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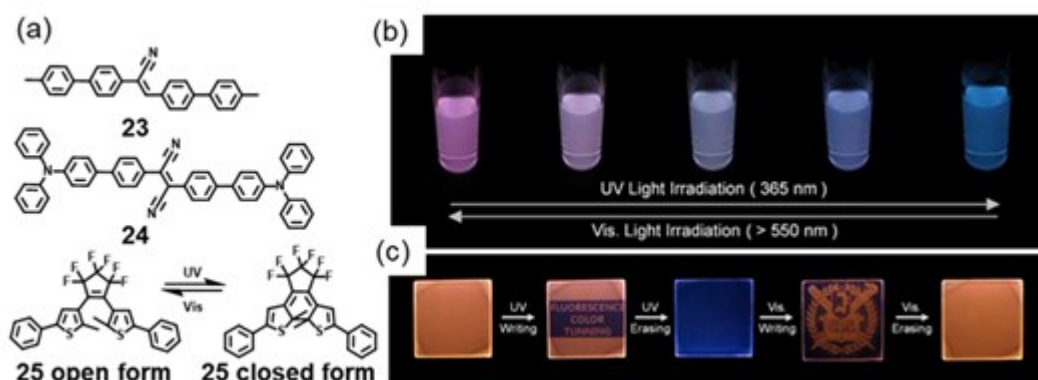
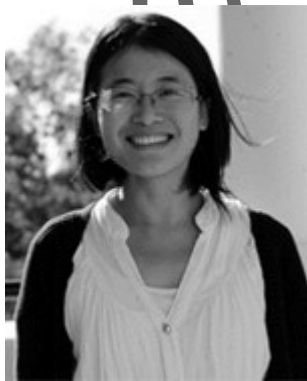


Figure 20. (a) Chemical structures of the fluorescent molecules: **23**, **24** and photochromic reaction of **25**. (b) Fluorescence images of the 23/24/25 nanoparticle suspension upon visible or UV light irradiation ($\lambda_{\text{ex}} = 365 \text{ nm}$). (c) Photo-responsive reversible fluorescence images of a 23/24/25-doped PMMA film system ($\lambda_{\text{ex}} = 365 \text{ nm}$). The orange-red and violet-blue regions represent regions irradiated with visible or UV light, respectively. Reproduced with permission.^[148] Copyright 2012, ACS.



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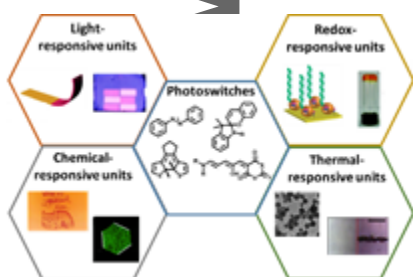
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a research focus on asymmetric catalysis. He then moved to California, where he worked in the area of total synthesis with Professor Larry E. Overman at the University of California, Irvine.

ToC text:

Multi-addressable architectures exhibit complex responsive behavior and are capable of sophisticated functions due to their synergistic interactions. This review summarizes recent developments in the area of multi-stimuli responsive architectures that leverage photoswitches as one of their key design features, with the focus on their applications in soft-materials.

ToC figure



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