Tuning the photoreactivity of photocycloaddition by halochromism[†]

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ABSTRACT

Harnessing the power of light for chemical transformation is a long-standing goal in organic synthesis, materials fabrication and engineering. Amongst all photochemical reactions, [2 + 2] photocycloadditions are inarguably the most important and most frequently used. These photo-reactions have green characteristics by enabling new bond formation in a single step procedure under light irradiation, without the need for heat or chemical catalysis. More recently, substantial progress has been made in red-shifting the activation wavelength of photocycloadditions in response to research trends moving towards green and sustainable processes, and advanced applications in biological environments. In the past 5 years, our team has further expanded the toolbox of photocycloaddition reactions that can be triggered by visible light. In our exploration of photochemical reactivity, we found that reactivity is often red-shifted compared to the substrate's absorption spectrum. Our efforts have resulted in red-shifted photochemical reactions, providing some of the lowest energy – and catalyst-free – photo-activated [2 + 2] cycloadditions (up to 550 nm). More recently, we introduced an additional level of control over such finely wavelength gated reactions by altering the pH of the reaction environment, thus exploiting halochromic effects to enhance or impede the photoreactivity of red-shifted [2 + 2] photocycloaddition reactions. In this account, we discuss the current state of halochromically regulated photochemical reactions and their potential in soft matter materials on selected examples.

Introduction

In June 1908, Giacomo Ciamician presented a comprehensive account of his work on photochemistry, mostly in collaboration with his associate Paul Silber, at the Société Française de Chimie (French Chemical Society) meeting,[1] illustrating his vision of employing light as green energy to fuel organic synthesis.[2] Among the series of photochemical reactions presented, an important group of bond forming reactions, including the dimerization of cinnamic acid, stilbene, and coumarin, were described as the initial reports of [2 + 2] photocycloaddition.[3] These new bond forming reactions have critical value in organic synthesis – they provide excellent atom economy and occur in a single step transformation under mild conditions that allow control of the follow-up processes. Ciamician's pioneering work has thus opened a vibrant research area of photocyclo-addition, and extensive information collected in the 1960s and 1970s further revealed the cleavage of the cycloadducts upon irradiation with shorter UV wavelengths, along with mechanistic work that provides an understanding of the characteristics of stilbene photocycloaddition chemistry.[4]

Towards the 1980s, research on photocycloaddition reactions has extended significantly from organic synthesis into soft matter materials. The characteristic of

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wavelength-controlled covalent bond formation and dissociation of reversible [2 + 2] photodimerization has enabled universal applications, e.g. the synthesis and modification of polymer architectures,[5,6] tuning properties of plastics,[7–9] hydrogels[10–12] and metal-organic frameworks,[13–15] as well as controlling biological processes *in situ* or *in vitro*.[16,17] More recently, the increasing interest in advanced applications under environmentally and biologically benign conditions has strongly enhanced the development of red-shifted reversible photochemical systems. In contribution to such endeavours, our team and others have introduced new [2 + 2] photocycloaddition reactions that can be triggered by long wavelength of visible light, up to green ($\lambda < 550$ nm) wavelength.[18,19] The longer activation wavelength further allows for their use in conjunction with other photochemical reactions, activated by shorter wavelength of light, in sequence-independent λ-orthogonal systems.[20–23]

While red-shifted absorption of the chromophores can be developed by engineering the chemical structure to expand the π-system via conjugation with aromatic systems, e.g. naphthalene,[24,25] anthracene,[26] pyrene,[19] or pyranocarbazole,[27] their photoreactivity can be further controlled by the environment. In particular, the λ-dependent reactivity and kinetics of the cycloaddition can be altered significantly when the chromophores are in crystal form[28], in confined environments,[29,30] or attached to a surface.[31,32] Furthermore, chromophores with halochromic properties, i.e. compounds that can change their absorbance reversibly at different pH levels, can have different photoreactivities depending on their protonation state. Such substances have important utility in λ-orthogonal systems where the pH switch can assist in the orthogonal initiation of two photochemical reactions, one of which is not pH-dependent, under irradiation of a single wavelength regime. In the current account, we discuss recent developments in the halochromic regulation of the photoreactivity of [2 + 2] cycloaddition reactions. Specifically, we focus on intermolecular photodimerization, rather than intramolecular photocycloaddition systems that have practical significance mostly in natural product synthesis.[4,33–35] We further highlight the potential applications of such photochemical systems in soft matter material design.

Halochromic enhancement of photodimerization in confined environment

The remarkable effect of acid on the regioselectivity of [2 + 2] photodimerization of *trans*-styrylpyridine, specifically the majority formation of the *syn* head-to-tail dimer, (Fig. 1*a*) was reported in the early 2000s.[36,37] Such a high regioselectivity is due to the preorientation of the pyridinium salt during the photocycloaddition, particularly the cation-π interactions between the pyridinium and aromatic rings that enable the molecules to arrange themselves in a head-to-tail pattern.[38,39] Further studies on these systems indicate that the strength of the cation π-interaction can be enhanced by increasing the size of the conjugated π-structures.[40] In 2017, Yamada and Nojiri noticed the acidic conditions provide the extended π-systems, such as nathylvinylpyridines, not only excellent regio- and stereoselectivity but also a red-shift (10–30 nm) in the absorbance, with a shoulder extending into the 400 nm region, thus enabling the photocycloaddition of the protonated species by visible light (Fig. 1*a*).[25]

Recently, we combined the highly conjugated π-system of pyrene with pyridine, establishing a new halochromic chromophore (pyren)vinylpyridine (PyPy) for red-shifted photocycloaddition.[41] Meticulous analysis of the PyPy reaction pathway under irradiation of various wavelengths revealed interesting characteristics that differ from the previously reported pyridine-based systems. In neutral conditions, *trans*-PyPy undergoes reversible photocycloaddition under blue light ($\lambda_{max} = 450$ nm) and UV light ($\lambda_{max} = 360$ nm) irradiation, respectively (Fig. 1*b*). The cycloaddition adducts [PyPy]$_2$ entail three main regioisomers (*anti*- head-to-tail: 10%, *syn*- head-to-tail: 37%, and *syn*- head-to-head: 53%) formed in 94% yield, together with a small amount (2%) of *cis*-PyPy. The protonated state PyPy^{H+}, induced by addition of trifluoroacetic acid, displays a red-shifted absorbance yet does not undergo photocycloaddition. Instead, we observed photoisomerization of PyPy^{H+} under irradiation at wavelengths up to 620 nm (Fig. 1*c*). The photoisomerization (*trans*- to *cis*-) was found to take place in common polar organic solvents, with the conversion in the range of 70–80%. The *cis*-form is retained after neutralization, displaying good thermal stability with no *cis*- to *trans*-isomerization after being left in the dark for 24 h. Subsequent photocycloaddition ($\lambda_{max} = 450$ nm) of the *cis*-form results in a higher regioselectivity, specifically the formation of *syn*- head-to-head (60%) and *anti*- head-to-tail (25%) as the major regioisomers.

When attaching the chromophores to a polymer chain to increase the proximity of the photoreactive moieties, we observed the photocycloaddition of the protonated PyPy^{H+} by green ($\lambda_{max} = 525$ nm) or orange ($\lambda_{max} = 590$ nm) light irradiation (Fig. 1*d*) and folding of the polymer chains, as evident by both size exclusion chromatography and NMR analysis of the polymers post-irradiation. In the neutral state, the polymer folding via photocycloaddition only occurred under irradiation at wavelength up to 450 nm. Clearly, the confined environment of a single polymer chain can overcome the restrictions blocking the photocycloaddition of the protonated PyPy^{H+} moiety. Our work thus opens up new opportunities in controlling the reaction pathways of the styryl moiety, and our preliminary demonstration in polymer folding indicates the applicability of the halochromic effect in tuning polymer architectures under irradiation of long wavelength visible light.
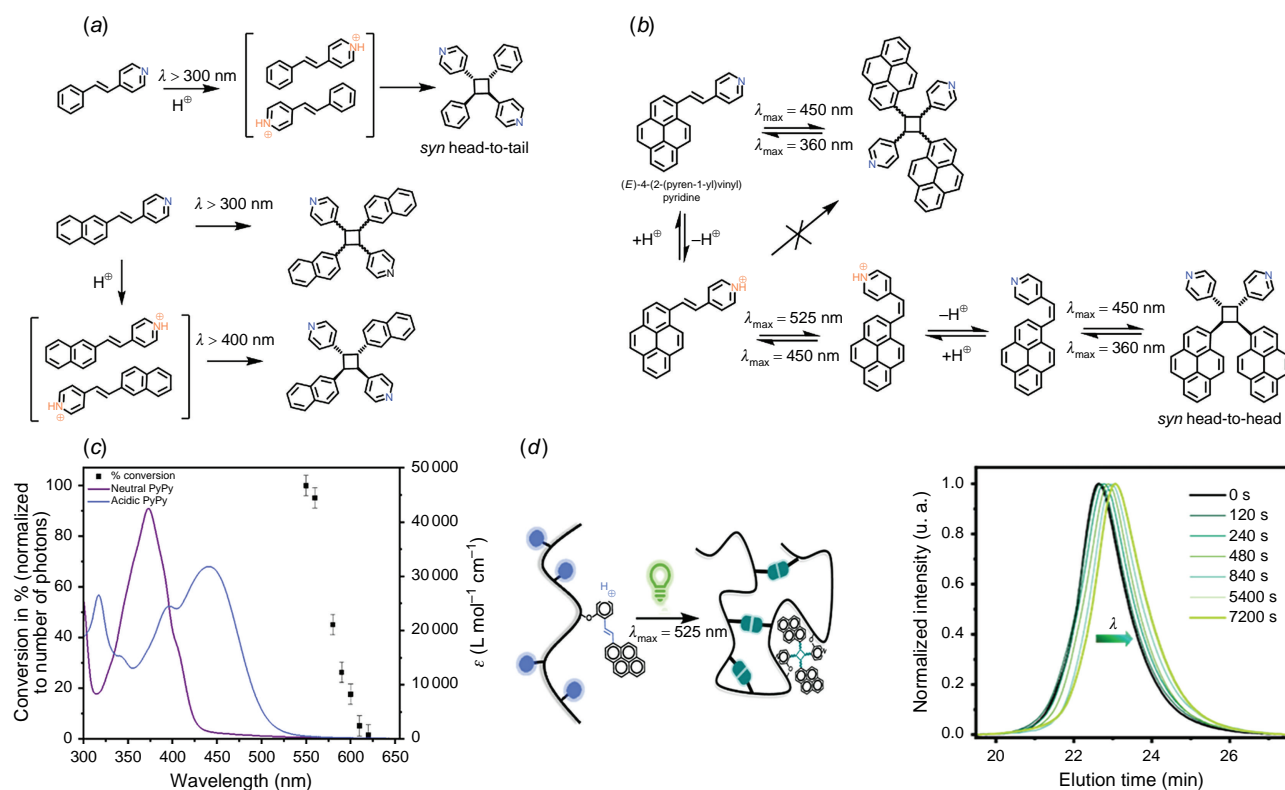
Fig. 1. Overview of the halochromic styrylpyridine derivatives with specific isomer distribution and red-shifted photoreactivity in their protonated state. (*a*) Protonation of the pyridine moiety resulting in controlled regioselectivity; when coupled with extended π-system such as phthalene the photodimerization can be triggered by visible light. (*b*) (Pyren)vinylpyridine (PyPy) displays complex photoreaction pathways, including reversible photocycloaddition and *trans-/cis*-isomerisation, and specific regioselectivity depending on its protonation state. (*c*) absorption spectra of PyPy showing a red-shift in the absorbance in acidic condition and action plot of the *trans*- to *cis*-isomerisation of protonated PyPy, showing a pronounced red-shift of the photochemical reactivity compared to the absorption spectrum. (*d*) In the confined environment which is a single chain polymer, the protonated PyPy undergoes photocycloaddition by green light ($\lambda_{max} = 525$ nm, left), indicated by the compaction of the polymer hydrodynamic radii evaluated by size exclusion chromatography (right).

Halochromic inhibition of photodimerization

The photochemical behaviors of heterocyclic nitrogen-containing stilbene derivatives can differ significantly depending on their structural arrangement, such as the number of nitrogens and their placement, and substituents on the aromatic rings. For example, styrylquinoxaline only undergoes reversible *trans-/cis*-photoisomerization (Fig. 2a);[42,43] while quinoline compounds could potentially participate in photocyclization in the *cis*-form, followed by oxidation.[44,45] However, these compounds do not show any photodimerization under full light irradiation in solution. Interestingly, the team of Fedorov reported that addition of two methoxy groups at the *para*- and *meta*-positions on the styryl component enables reversible [2 + 2] photocycloaddition, with exclusive formation of the *syn* head-to-head isomer out of 11 possible regioisomers (Fig. 2a).[46] The authors proposed that the head-to-tail dimer organization of dimethoxystyrylquinoxaline in solution is due to the dipole interaction between the donor dimethoxyphenyl

moiety of one molecule and the acceptor quinoxaline residue of the other one, enabling the formation of the cycloadduct under irradiation of UV light ($\lambda_{max} = 365$ nm).

In the absence of methoxy substituents, [2 + 2] photodimerization of styrylquinoxaline can take place in Langmuir-Blodgett (LB) films due to the two-dimensional confined environment.[47,48] In this case, molecular preorientation is promoted by side-to-side packing of the amphiphilic (hydrophilic styrylquinoxaline head and hydrophobic alkyl chain) molecules, forming exclusively *syn* head-to-head dimer adducts.[49] While the halochromic properties of styrylquinoxaline LB films have been widely investigated for applications in sensors, only recently Lu and co-workers discovered that the dimerization rate was significantly reduced when the LB films were exposed to HCl gas.[50] Therefore, it is likely that the protonated forms disrupt the head-to-head aggregated structures of the monolayer, preventing the photodimerization processes.

In light of the recent reports on photocycloaddition of the styrylquinoxaline (SQ) derivatives, we sought to employ
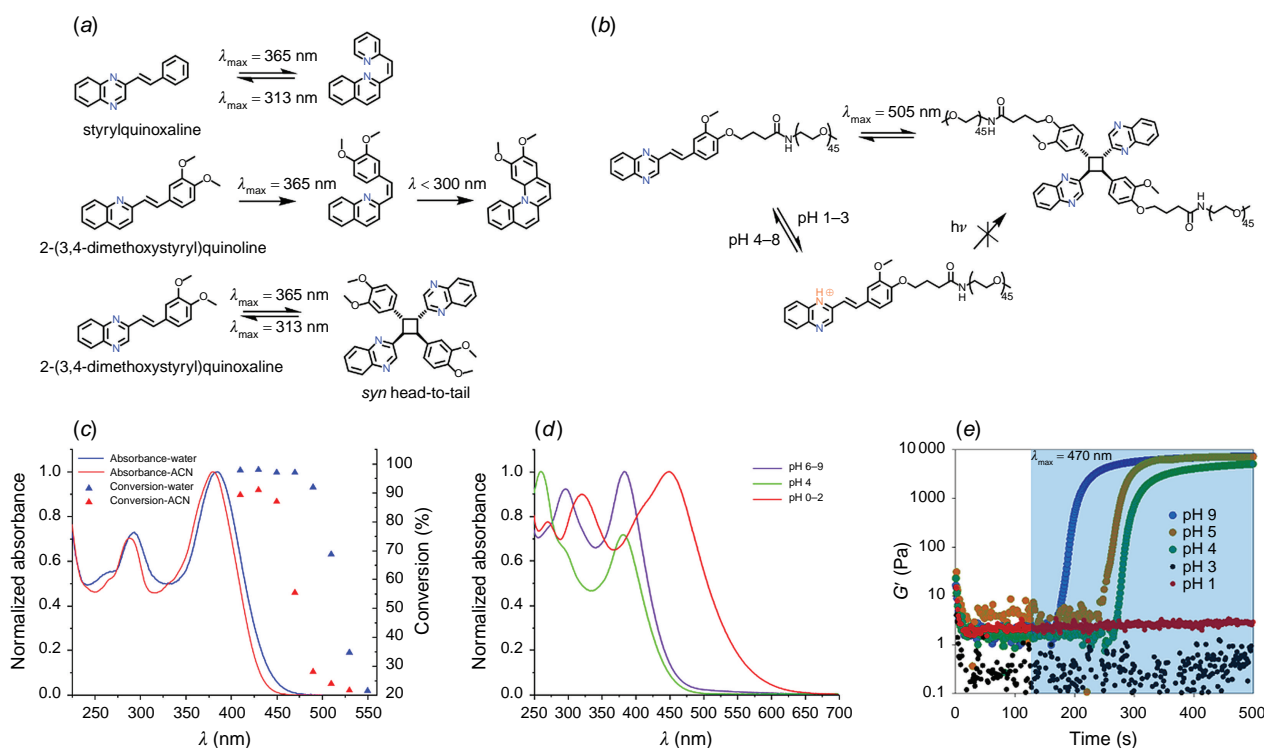
Fig. 2. Photochemical pathways of styrylquinoxaline derivatives and their application in polymer ligation. (*a*) Diverse photo-chemical transformation of N-containing heterostilbenes, including *trans-*/*cis-* photoisomerisation, photocyclization, and photo-cycloaddition, all depending on the nitrogen placement and substituents on the styryl moiety. (*b*) PEG with (2,3-dimethoxy) styrylquinoxaline (SQ) endgroup displays photodimerization under irradiation with green light ($\lambda < 520\,nm$) in water, and the photochemical reaction is inhibited when the moiety is in its protonated state. (*c*) In its neutral state, the SQ function shows a red-shift in photoreactivity (~40 nm) in water compared to acetonitrile. (*d*) When protonated at pH < 3, the SQ function shows a red-shift (~100 nm) in its absorbance. (*e*) Crosslinking of an 8-armed PEG functionalized with SQ under blue light ($\lambda_{max} = 470\,nm$) irradiation followed by rheological measurement demonstrates the pH control over the gelation processes, with inhibition of crosslinking under acidic (pH ≤ 3) conditions.

such chromophores in polymer ligation and crosslinking. Our main interest lies in biological applications, and we thus developed a synthetic protocol to attach the SQ chromophore to a water soluble poly(ethylene glycol) (PEG), while retaining the (2,3-dimethoxy)styryl motif (Fig. 2b).[51] By mapping the photodimerization as the function of wavelength using a monochromatic tuneable laser system, we found green light ($\lambda < 520\,nm$) can be used to trigger photocycloaddition in an aqueous environment (Fig. 2c). Furthermore, acidic conditions (pH < 4) result in a red-shift in the absorption (~100 nm) of the compound in solution (Fig. 2d), and inhibition of the photocycloaddition. By attaching the styrylquinoxaline to an 8-armedPEG, we were able to form hydrogels by irradiation of the polymer solution with blue or green light, and the photo-crosslinking process was further controlled by adjusting the pH of the solution (Fig. 2e).

To further red-shift the activation wavelength for photodi-merization, we developed a new heterocyclic styryl derivative with three nitrogen centres, namely styrylpyrido[2,3-b] pyrazine (SPP) (Fig. 3a).[52] In a neutral aqueous environment,

the SPP can participate in [2 + 2] photocycloaddition under irradiation of wavelength up to 550 nm, which is the longest wavelength employed in photocycloaddition in solution and without the assistance of confined environment conditions. Critically, replacement of the phenyl with a pyrido subunit results in the increase in the pK$_a$ of the resultant compound (SQ pK$_a$ = 0.6; SPP pK$_a$ = 1.15), and consequently enhancement of the halochromic response. When mapping the photo-dimerization ratio as a function of pH, we observed a significant decrease in the monomer conversion when pH was switched from 7 to 6 (~50 to ~20%) under identical irradiation condition at $\lambda_{max} = 480\,nm$. This enhanced halo-chromic response enables the use of an internal pH regulator, which was a water soluble spiropyran photoacid generator (PAG),[53] to restrict the activation wavelength of photo-dimerization (Fig. 3a). Under excitation at $\lambda = 400–510\,nm$, the PAG undergoes photoisomerization and protonates the SPP function, limiting its photodimerization to only under green light ($\lambda = 520–550\,nm$) irradiation.

Taking advantage of the restricted activation wavelength of SPP in the presence of the PAG, we established a
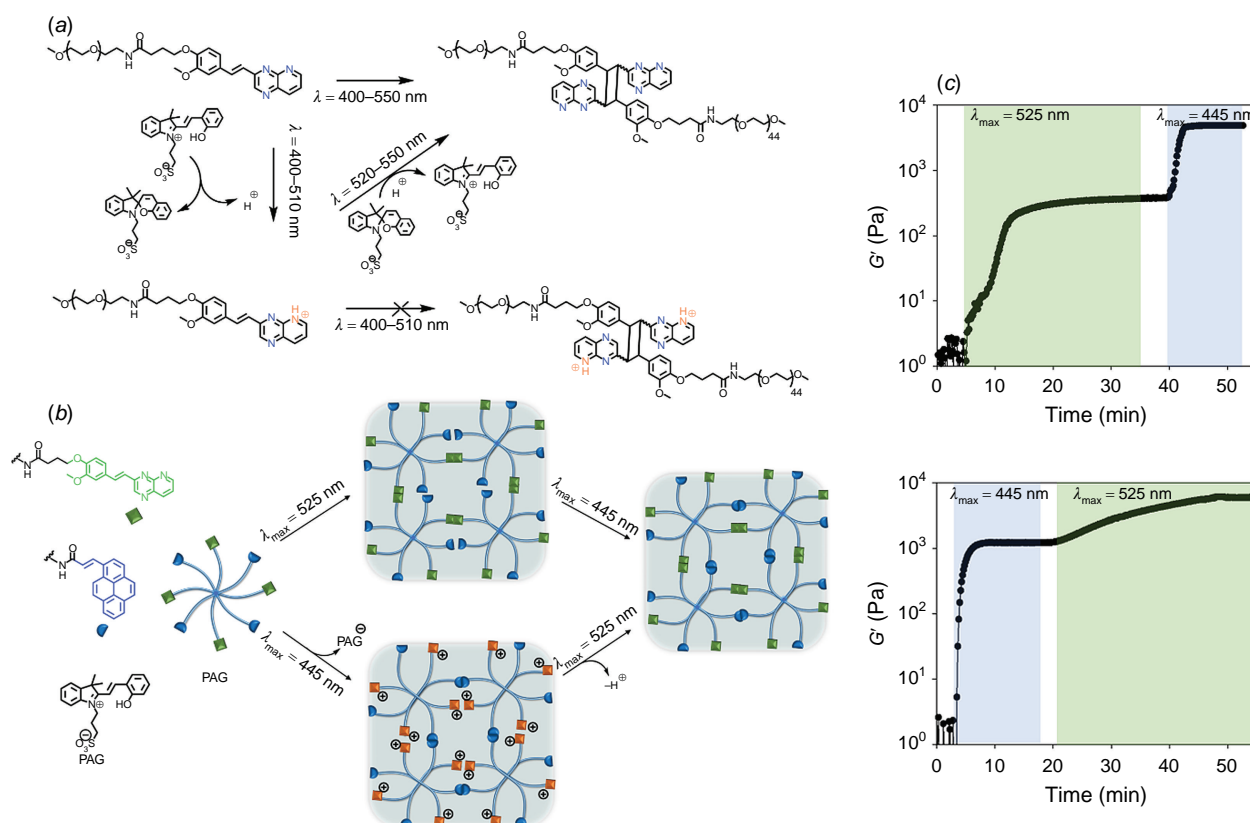
Fig. 3. λ-orthogonal activation of two photodimerization processes by utilizing the halochromic properties and a photoacid generator (PAG). (*a*) The styrylpyrido[2,3-b]pyrazine (SPP) moiety can undergo photodimerization under irradiation at λ = 400–550 nm, and the activation window can be narrowed to λ = 520–550 nm in the presence of a PAG, which can produce acidic environment under irradiation at λ = 400–510 nm; outside the 400–510 nm window the SPP exists in neutral form. (*b*) The SPP (green) can be attached to an 8-armed PEG together with a non-halochromic acrylamidylpyrene, establishing a polymer that can be crosslinked by either blue (λ_max = 445 nm, via dimerization of the AP), or green (λ_max = 525 nm, via dimerization of the SPP) irradiation, in the presence of the PAG. (*c*) Rheological assessments of the photo-crosslinking processes demonstrate that gelation can be induced by either blue or green light irrespective of irradiation sequences.

λ-orthogonal photoactivation of two photodimerization processes, one of which is the photocycloaddition of non-halochromic acrylamidylpyrene (AP, Fig. 3b) under irradiation at λ = 410–490 nm. We integrated this photochemical system into a polymer crosslinking concept, and demonstrated the λ-orthogonal stiffening of hydrogel materials by either blue or green light (Fig. 3c). We expect that all chromophores, including the PAG, SPP, and AP can be covalently integrated into a single system for modulation of mechanical properties. The exclusive use of visible light to finely tune the moduli of hydrogel materials is highly attractive for applications in cell mechanotransduction studies.

Concluding remarks

It is evident that the herein described progress in halochromic tuning of photochemical transformations of the heterocylic N-containing stilbene represents a valuable tool for soft matter materials modification, with applications in biological environments. Critically, the halochromic control over the photochemical transformation can provide *additional orthogonal control* over two or more spatiotemporal elements, which is highly beneficial for regulation of multiple biological events, such as enzymatic signalling pathways,[54] microRNA interactions in cellular processes,[55] or microorganism growth.[56] Currently, we are investigating the potential of photoinduced [2 + 2] cycloaddition for DNA modification and exploiting precision photochemistry for tracing processes by live-tagging cells. Given that chromaticity is highly pH dependent, we submit that the prospects for establishing sensitive and biorthogonal halochromic systems are realistic. Therefore, it will be interesting to establish if the pH gated control of photochemical reactivity can be exploited in living systems, where pH levels tend to site- and morbidity dependently vary (e.g. in cancerous tissue, where cancer cells have a lower extracellular pH of ~6.7 compared to pH of 7.4 in

normal cells).[57] For this to occur, even finer control of photochemical reactivity in response to even slight pH changes needs to be established.

In addition to the opportunities available for halochromic control in biological systems, halochromic control over photo-induced coupling can be exploited in sensor applications, where system status can be potentially read-out by photo-chemical reactivity responses.[48] Thus, increasing the sensitivity of the halochromic response will also be critical for such applications outside the biological arena. Finally, it might be possible to dual gate photochemical reactivity not only with halochromaticity, but with an additional gate such as supra-molecular templating[58] or organocatalysis activation,[59] opening avenues to safe-guarded photochemical responses for the forward reaction but possibly also for the reverse. Such dual gated photochemically induced debonding reactions could find use in fail-safe adhesives,[60] where two triggers have to come to together before release occurs.

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