

# Wavelength Orthogonal Photodynamic Networks

Vinh X. Truong<sup>+,\*</sup>[a, b] Katharina Ehrmann<sup>+,\*</sup>[a, b] Maximilian Seifermann,<sup>[c]</sup> Pavel A. Levkin,<sup>\*,[c]</sup>  
and Christopher Barner-Kowollik<sup>\*,[a, b, d]</sup>

**Abstract:** The ability of light to remotely control the properties of soft matter materials in a dynamic fashion has fascinated material scientists and photochemists for decades. However, only recently has our ability to map photochemical reactivity in a finely wavelength resolved fashion allowed for different colors of light to independently control the material properties of polymer networks with high precision, driven by monochromatic irradiation enabling orthogonal reaction control. The current concept article highlights the progress in visible light-induced photochemistry and explores how it has enabled the design of polymer networks with dynamically

adjustable properties. We will explore current applications ranging from dynamic hydrogel design to the light-driven adaptation of 3D printed structures on the macro- and micro-scale. While the alternation of mechanical properties via remote control is largely reality for soft matter materials, we herein propose the next frontiers for adaptive properties, including remote switching between conductive and non-conductive properties, hydrophobic and hydrophilic surfaces, fluorescent or non-fluorescent, and cell adhesive vs. cell repellent properties.

## Introduction

Nature demonstrates the transformative power of photochemistry, enabling life on our planet.<sup>[1]</sup> It is thus no surprise that unravelling photochemical reaction mechanisms has been a research focus for hundreds of years.<sup>[2]</sup> A particularly attractive feature of light-driven chemistry is its ability to deliver highly precise packets of energy to specific regions of matter, in the case of two photon absorption even with theoretically unlimited resolution.<sup>[3]</sup> Coupled with the ability of a range of

chemical reactions to undergo reversible bond formation, these properties open a plethora of opportunities for the design of soft matter materials whose properties can be adjusted dynamically by exposing them to different colours and intensities of light, constituting remote control of material properties.<sup>[4]</sup> Fine control of material properties is only possible based on detailed data regarding the reactivity of photochemical processes as a function of wavelength. We have recently summarized the current understanding in the field, based on the in-depth analysis of photochemical reactions by so-called action plots, which map covalent bond formation wavelength-by-wavelength, allowing for a direct comparison with the extinction spectrum of the chromophore in question.<sup>[5]</sup> Such a detailed analysis shows that the wavelength dependent reactivity profiles do not necessarily follow the extinction spectrum, typically exhibiting a distinct red-shift of the reactivity.

The advances in our understanding of bond forming/breaking/switching photochemical reactions in a wavelength resolved fashion have opened up unique opportunities for dynamic soft matter materials design, specifically in the realm of polymer networks, where polymer chains are tethered to each other through covalent connections. These connections render the polymeric material insoluble and impart specific material properties. We refer the interested reader to the existing excellent and comprehensive reviews in the field.<sup>[6]</sup> Herein, we will focus on networks where these covalent connections can be chemically influenced by light in an ideally reversible fashion. Figure 1 displays such a situation and summarizes the most widely used photochemistries that have been exploited in photodynamic network design.

Two approaches to network formation can be differentiated: (i) thermal network formation, where photochemical units are incorporated in the thermally curable monomers, which can be installed in variable amounts throughout the network; and

[a] Dr. V. X. Truong,<sup>+</sup> Dr. K. Ehrmann,<sup>+</sup> Prof. Dr. C. Barner-Kowollik  
School of Chemistry and Physics  
Queensland University of Technology (QUT)  
2 George Street, Brisbane, QLD 4000 (Australia)  
E-mail: truongvx@qut.edu.au  
christopher.barnerkowollik@qut.edu.au

[b] Dr. V. X. Truong,<sup>+</sup> Dr. K. Ehrmann,<sup>+</sup> Prof. Dr. C. Barner-Kowollik  
Centre for Materials Science  
Queensland University of Technology (QUT)  
2 George Street, Brisbane, QLD 4000 (Australia)

[c] M. Seifermann, Prof. Dr. P. A. Levkin  
Institute of Biological and Chemical Systems  
Functional Molecular Systems (IBCS-FMS)  
Karlsruhe Institute of Technology (KIT)  
Hermann-von-Helmholtz Pl. 1, 76344 Eggenstein-Leopoldshafen (Germany)  
E-mail: pavel.levkin@kit.edu

[d] Prof. Dr. C. Barner-Kowollik  
Institute for Nanotechnology (INT)  
Karlsruhe Institute of Technology (KIT)  
76021 Karlsruhe (Germany)

[\*] These authors contributed equally.

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(ii) network formation that is photochemically induced, where the photochemically reactive units are utilized for polymerization. These bond-forming photochemical reactions can also be utilized in post-modifications along with photochemical isomerization reactions. While all photochemical ligation and degradation reactions can potentially be employed in photodynamic networks, wavelength orthogonality can only be achieved if a broad range of the optical spectrum is utilized for competing reactions. The latter approach, while highly attrac-

tive – as the networks can be formed via light-driven 3D printing processes thus enabling free form structures – requires the writing wavelength to be fully orthogonal to the wavelength of activation of the photoreversible units present in the resist.

Wavelength orthogonality between two photochemical reactions is defined as the pathway independent ability to activate one of these reactions without inducing conversion of any other reaction, no matter in which order the different

Vinh X. Truong received his PhD degree in Bioengineering from the University of Queensland, Australia in 2011, followed by a postdoctoral period in the group of Prof Andrew Dove at Warwick University. He returned to Australia as a Research Fellow, and was appointed a Lecturer in Biomaterials at Monash University. In 2020, Vinh joined the Soft Matter Laboratory at QUT to develop advanced photochemical systems for (bio)materials engineering. He has published over 50 papers in high profile journals. His current research focuses on redshifted photochemistry, cell culture scaffolds, and antimicrobial coatings.



Katharina Ehrmann graduated from TU Wien in 2020, where she investigated polymeric biomaterials. She then continued as a postdoc in the group of Prof Robert Liska at TU Wien shifting her research focus towards photopolymers for additive manufacturing. In 2021, Katharina joined Prof Christopher Barner-Kowollik's team at QUT as a Research Fellow, where she continues to work on light-triggered polymer networks. Katharina has been awarded the Dr. Maria Schaumayer prize for her dissertation, co-authored 16 publications and presented her work at several national and international conferences.



Maximilian Seifermann studied Chemistry at the Karlsruhe Institute for Technology and obtained his Master of Science in Organic Chemistry. He is currently working as a PhD candidate at the Levkin research group with the focus on miniaturized chemistry, surface chemistry and soft materials.

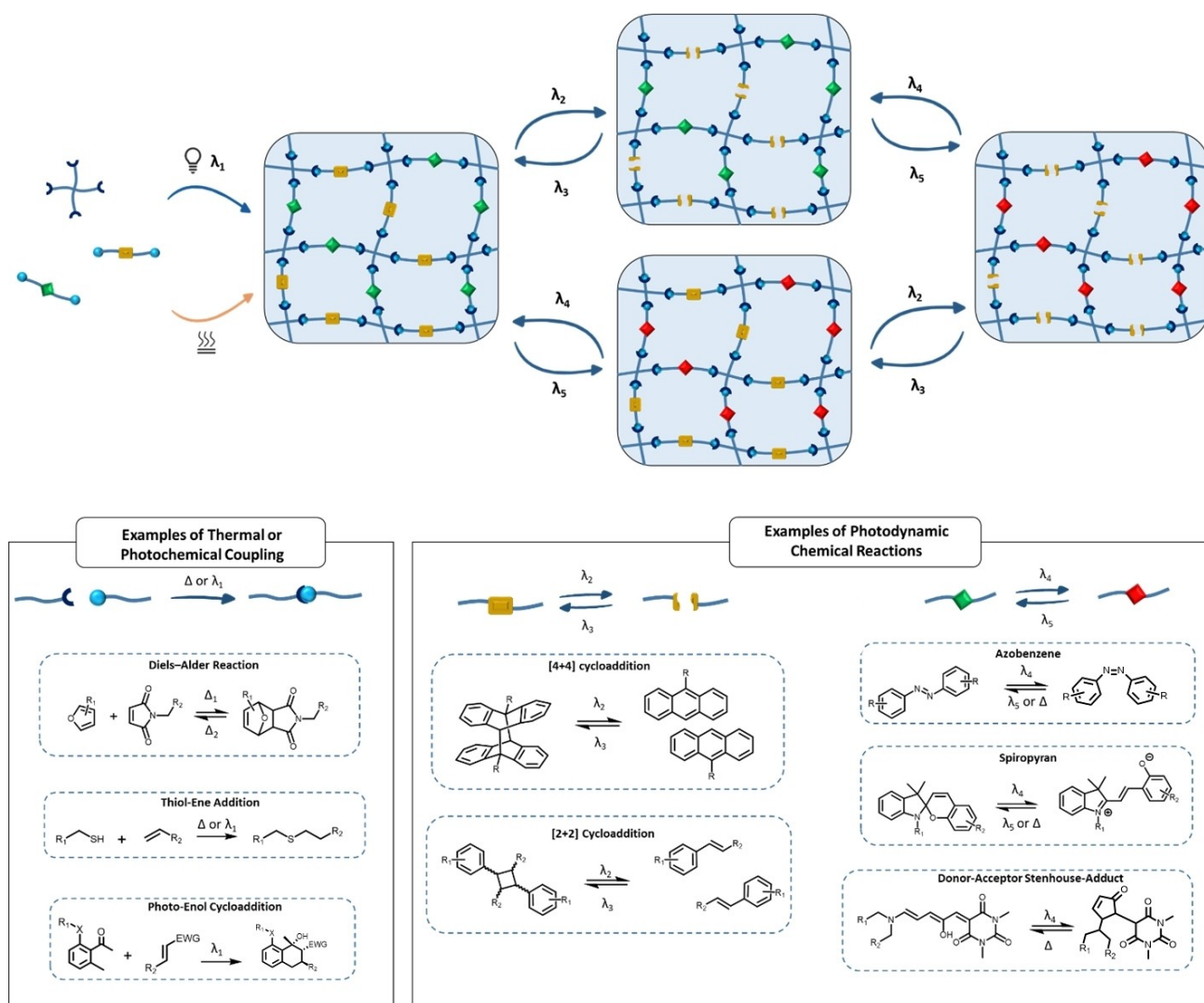


Pavel Levkin graduated from the Institute of Fine Chemical Technology, Moscow and obtained his Ph.D. in Organic Chemistry from the University of Tübingen in Germany, followed by postdoctoral work at the University of California, Berkeley. Pavel joined Karlsruhe Institute of Technology (KIT) as a group leader in 2010 and accepted Heisenberg professorship in 2020. Currently Pavel is the head of the Biofunctional Materials Systems research group at the Institute of Biological and Chemical Systems (IBCS-FMS) and Institute of Organic Chemistry (IOC) at the KIT. He received the Ewald-Wicke Prize in 2014 and the Heinz-Meyer Leibnitz Prize in 2015. He is also recipient of both Helmholtz Junior research group grant and the ERC Starting Grant. Pavel is the cofounder of ScreenFect GmbH and Aquarray GmbH. His research focuses on the development of functional and responsive materials, and surfaces for biomedical and biotechnological applications.



A macromolecular photochemist and graduate from Göttingen University, Christopher Barner-Kowollik joined the University of New South Wales in early 2000 rising to co-lead the Centre for Advanced Macromolecular Design. He accepted a professorial chair at the KIT in 2008, where he established and led a German Research Council funded Centre of Excellence. In 2017, he established QUT's Soft Matter Materials Laboratory. He leads and supports highly collaborative large teams, authoring over 700 peer-reviewed publications in leading journals. Christopher's research achievements have been recognised by a wide array of national and international awards including the coveted Erwin Schrödinger Award of the Helmholtz Association, the United Kingdom Macro Medal, the European Polymer Federation Prize as well as awards by the Australian Academy of Science, the Royal Australian Chemical Institute and the Royal Society of New South Wales, an ARC Professorial Fellowship and Laureate Fellowship.





**Figure 1.** Conceptual scheme (top) of photodynamic networks that can be formed via thermal- or light-induced crosslinking, during which photoreversible chromophores are incorporated within the networks, enabling switching of chemical and physical properties of the resultant networks by highly specific wavelengths of light. Examples (bottom) of chemical reactions, including chemical coupling (left) and reversible photochemical transformations (right), which can be employed in the top scheme.

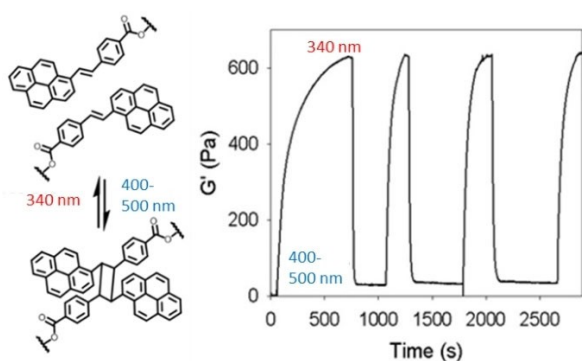
colours of light are applied. While full orthogonality refers to a set of reactions, which can be conducted mutually exclusively in their respective reactivity ranges regardless of the order in which the reactions are conducted, semi-orthogonal reaction sets contain at least one reaction, which has an overlapping reactive range with other reactions. Such reaction sets can therefore only be performed exclusively if a certain order of the reactions is maintained. The type of orthogonality can be predicted through the compatibility of the reactants' action plots. These depict the wavelength-resolved reactivity of a reactant and do not necessarily coincide with the respective absorption spectrum.<sup>[5]</sup> Fully orthogonal systems thus require ideally non-overlapping action plots or at least large differences between quantum yields of the reactions if there is some overlap. While all photochemical ligation and degradation reactions can potentially be employed in photodynamic networks, wavelength orthogonality can only be achieved if a

broad range of the optical spectrum is utilized for competing reactions, since particularly the high-energy UV-range is unsuitable for full orthogonality in most reaction sets. Therefore, we particularly highlight red-shifted photochemical reactions with low UV-responsiveness, which are still scarce due to two main reasons. Firstly, synthetic challenges such as multi-step synthetic procedures and solubility limit the potential for scale-up and applicability up to now. Secondly, the quantum yield typically decreases for reactions in the visible range. In soft matter materials applications, the use of long wavelength visible light can minimize the formation of free radicals and side reactions, such as photo-oxidative cleavage products, often generated by UV-light irradiation.

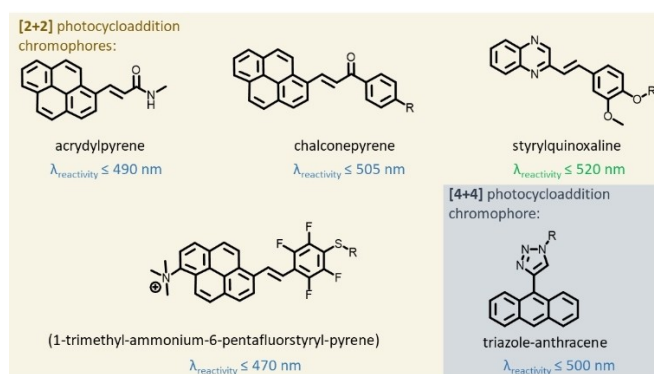
## Light-induced Tuning of Mechanical Properties

## Photocycloadditions

Dynamic networks whose structures can be reorganized by light have been extensively investigated for smart materials applications, including optically healable plastics and soft robotics.<sup>[7]</sup> Such applications often utilize photoreversible pericyclic reactions, such as [2 + 2] and [4 + 4] photocycloadditions, whose addition and reversion are activated by disparate wavelengths. Interestingly, the earliest report of a chromophore undergoing photocycloaddition by visible light dates to 1980,<sup>[8]</sup> but only in 2016 the reported chromophore, styrylpyrene, (Figure 2) was employed by Doi and co-workers in DNA crosslinking.<sup>[9]</sup> Here, the authors demonstrated the crosslinking of styrenepyrene-tethered DNA by light of  $\lambda_{\text{max}}=455$  nm, and reversion by UV light of  $\lambda_{\text{max}}=340$  nm. Subsequently, Truong et al. prepared a 4-arm poly(ethylene glycol) containing styrylpyrene end groups, which can crosslink to form a hydrogel by visible light ( $\lambda_{\text{max}}=455$  nm).<sup>[10]</sup> These authors noted that the photodegradation at  $\lambda_{\text{max}}=340$  nm is highly dependent on the crosslinking density of polymer networks, with light-induced



**Figure 2.** Reversible [2 + 2] photocycloaddition of red-shifted styrylpyrene and its application in the wavelength-orthogonal crosslinking and degradation of a PEG hydrogel, followed by photorheological assessment. Reproduced with permission from Ref. [10]. Copyright (2018) American Chemical Society.



**Scheme 1.** Chemical structures of red-shifted chromophores that can undergo [2 + 2] or [4 + 4] photocycloadditions.  $\lambda_{\text{reactivity}}$  refers to the wavelength range at which the chromophore is reactive.

bond cleavage more efficient at lower crosslinking density (Figure 2). Notably, the visible light-induced photocycloaddition of styrylpyrene was shown to be non-toxic to living cells, displaying potential of the system in cell biology research.

Within the last five years, the library of chromophores that can undergo [2 + 2] cycloaddition by light at  $\lambda=400$ –520 nm has been expanded moderately, with most of the new chromophores based on the core structure of pyrene (Scheme 1).<sup>[11]</sup> A notable non-pyrene chromophore is styrylquinoxaline, which displays, in addition to green light-responsive reactivity, a pH-dependence related to its photoreactivity. Except for the newly reported chalconepyrene, all other chromophores have been employed in polymer crosslinking for hydrogelation by visible light.<sup>[12]</sup> However, the reversion by UV light ( $\lambda=340$ –365 nm) is not efficient in all cases and photodegradation of these hydrogels has not been reported. Nevertheless, detailed mapping of the photoreactivity via action plot studies of these red-shifted chromophores opens up opportunities for the design of orthogonal reaction systems. In particular, some of our team have demonstrated the wavelength-dependent stiffening of hydrogels containing two photoreactive moieties, of which the acrydylpyrene is reactive at longer wavelengths than the styrylpyrene.<sup>[11c]</sup>

In contrast to [2 + 2] photocycloadditions, accounts of catalyst-free and red-shifted [4 + 4] photocycloadditions are scarce, with only one reported chromophore based on an anthracene core (Scheme 1).<sup>[13]</sup> Here, the red-shift in photoreactivity is induced by an electron-rich triazole moiety at the 9-position of the anthracene ring. Photocycloaddition of the triazole anthracene by visible light (400–500 nm,  $I=10$  mW cm<sup>-2</sup>), and the stiffening of the network can be regulated by controlling the time of irradiation.<sup>[13a]</sup> However, reversion of the dimers is highly inefficient, and the authors report that the hydrogels could not be degraded by UV light at 365 nm.

Collectively, although a range of red-shifted chromophores have been introduced for visible light-enabled photocycloadditions, the decoupling of dimers by UV light is highly inefficient within hydrogel networks. Since the hydrogels reported above are mainly targeted for cell culture applications, short wavelength UV light ( $\leq 340$  nm) was not considered due to the harmful effect of such UV wavelength on living cells. Outside of biology-related applications, incorporation of these chromophores into plastics is a potential avenue for applications in, for example, light-induced healing or shape-changing soft matter materials.

## Azobenzene isomerization

Photoisomerization of the azobenzene moiety has been extensively employed in the light-induced reconfiguration of materials' structures, and applications of UV/blue light switching of azobenzene derivatives in polymeric materials are well-documented in an excellent review by Goulet-Hanssens and co-workers.<sup>[14]</sup> Red-shifting of the azobenzene absorbance can be

induced by placing different substituents, such as thiol,<sup>[15]</sup> methoxy,<sup>[16]</sup> or halogen<sup>[17]</sup> at the *ortho*- or *para*- positions on the phenyl rings. *Ortho*-halogen-substituted azobenzenes not only have excitation wavelength (*trans*- to *cis*-) extended into the NIR region, but also have much slower thermal relaxation (*cis*- to *trans*-) rates (tetra-*ortho*-fluoro azobenzene has a thermal half-life of two years) compared to non-substituted azobenzenes.<sup>[17]</sup> This feature is highly attractive as the two isomers display well-separated absorption bands, and the photoswitching of both forms is addressable in the visible light regime with good quantum yield. So far, these red-shifted azobenzenes have mostly been used in photoreversible hydrogelation, either by a reversible polarity change of amphiphilic polymers (Figure 3A)<sup>[18]</sup> or by complexation with  $\beta$ -cyclodextrin (Figure 3B) for tuning the viscoelasticity of the hydrogels.<sup>[19]</sup> More recently, Kalow and co-workers utilised the photo-switching of these red-shifted azobenzenes for tuning the boronic acid ester equilibrium, with the *cis*-form providing significantly higher binding affinity of the boron towards diol compounds.<sup>[20]</sup> The authors further demonstrated photodynamic control of the viscoelastic properties of PEG-based hydrogels by red and blue light.<sup>[20b]</sup> The azobenzene-incorporated hydrogels have low mechanical strength and readily dissolve in aqueous environments, making them attractive for controlled drug delivery systems. Incorporating these red-shifted azobenzenes into crosslinked structures, as shown in Figure 1, will significantly extend their utility in biomaterial applications, for example mechanotransduction studies or shape-changing soft materials.

### Protein-based photodynamic crosslinking

Light-driven supramolecular assembly of photoresponsive proteins, such as phytochrome and Dronpa, have been investigated for light-gated tuning of biomimetic hydrogels' stiffness. When excited with green light (500 nm), the monomeric mutant fluorescent Dronpa145 switches to the bright state and exists in

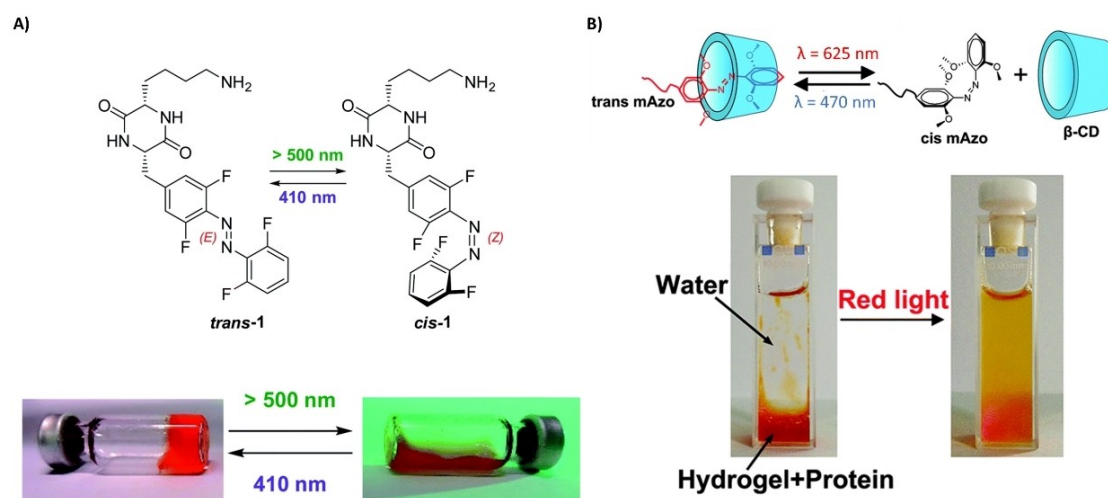
the tetramer form, which can be reverted to monomer by blue light ( $\lambda_{\text{max}} = 400 \text{ nm}$ ).<sup>[21]</sup> Incorporating Dronpa145 into hydrogel networks enables photodynamic tuning of the mechanical properties via wavelength-orthogonal oligomerization/dissociation of the protein.<sup>[21–22]</sup>

More recently, Hörner and co-workers incorporated an engineered cyanobacterial phytochrome 1 into a PEG hydrogel, crosslinked via thiol-vinylsulfone Michael addition, resulting in a network whose stiffness can be adjusted by wavelengths at 660 nm and 740 nm, respectively (Figure 4).<sup>[23]</sup> It is noted that the synthesis protocol for such phytochrome-based hydrogels does not allow for encapsulation of living cells due to the long gelation time. Nevertheless, the responsiveness towards long wavelength visible and NIR light with high tissue penetration properties has potential for *in vivo* applications, for example photomodulation of biomaterials properties deep within tissues.

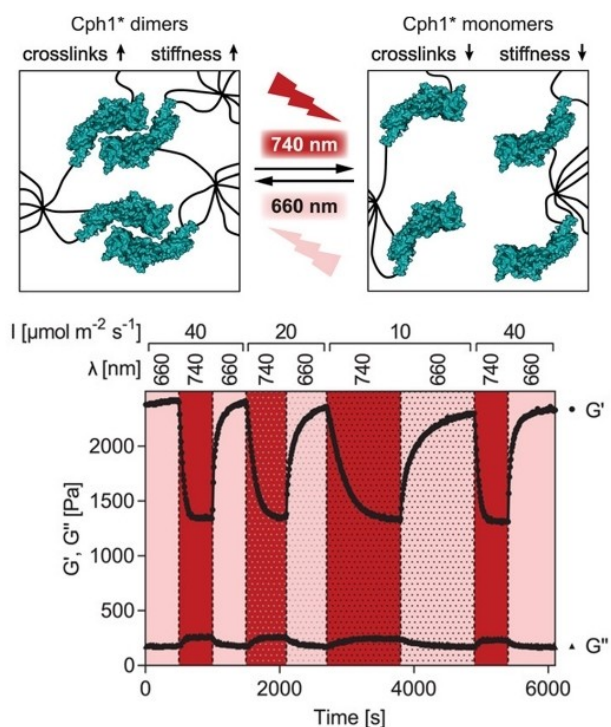
## Light-induced Modulation of Polarity

### Spiroyrans

Since the discovery of spiroyrans photochromism in 1952, these photoswitches have found their ubiquitous use in numerous material applications, including sensors, actuators, and responsive microfluidic devices.<sup>[24]</sup> The structural change of spiroyrans under visible light irradiation is accompanied by a significant change in its dipole moment, varying from 4–6 D (closed spiroyrans form) to 20 D or above (open merocyanine form) (Figure 1).<sup>[25]</sup> Such a profound change has been utilized in polymer networks for switching of hydrophobicity/ hydrophilicity, enabling changes in the physical conditions of the polymers, which are for example applied in shape-changing polymers.<sup>[7]</sup> In particular, the combination of acidic functionalities and spiroyrans-moieties allowed the isomerization from the protonated merocyanine (MCH<sup>+</sup>) to the cyclic spiroyrans



**Figure 3.** Application of red-shifted azobenzenes in photoreversible hydrogelation by A) assembly/dissociation of amphiphilic peptides; reproduced with permission from Ref. [18]. Copyright (2018) Wiley-VCH GmbH. B) complexation with  $\beta$ -cyclodextrin.<sup>[19b]</sup>



**Figure 4.** Hydrogel network containing cyanobacterial phytochromes that can reversibly dimerize by irradiation with red and NIR light (top). Photo-rheological data showing the reversible switching of the hydrogel stiffness under irradiation of red/NIR light; reproduced with permission from Ref. [22] Copyright (2019) Wiley-VCH GmbH.

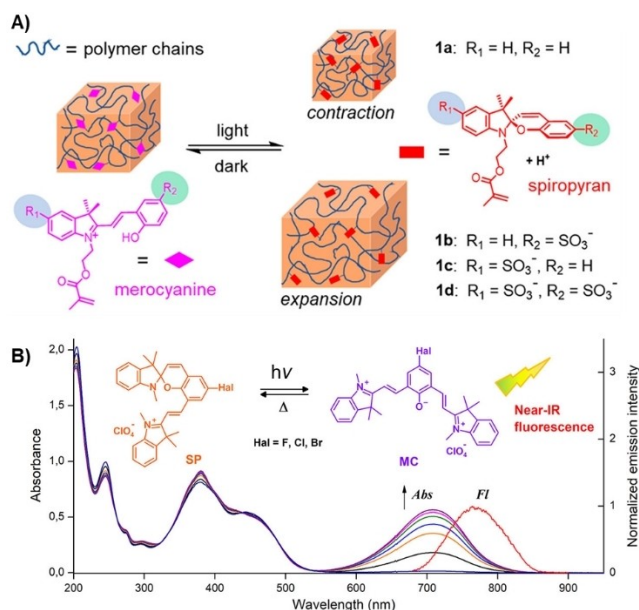
through irradiation with visible light, leading to the expansion or contraction of the materials (Figure 5A).<sup>[26]</sup> It was shown that gels with controlled volume transition can be used as valves in microfluidic devices, blocking channels through controlled size changes.<sup>[27]</sup> The combination of expansion and contraction in one material allowed for a controlled network deformation, enabling self-folding or unidirectional motion of materials.<sup>[28]</sup> In these applications, the reversed reaction is triggered by either UV light or thermal isomerizations. It is noted that the solvent has a strong influence on the stability of each isomer, with the open merocyanine and its acid form more favoured in aqueous environments, whereas the ring-closed form spiropyran is more stable in organic solvents such as acetonitrile.

Spiroyrans with red-shifted absorbance, via a conjugated structure with chromene moiety (Figure 5B), have only recently been reported,<sup>[29]</sup> and these compounds are yet to be incorporated into polymer networks.

## Light-induced Modulation of Optical Properties

### Diarylethenes

Chromophores that can undergo light-induced reversible color changes hold key potential in the manufacturing of optical storage systems, optoelectronic devices, sensors, actuators, and biological imaging.<sup>[30]</sup> Diarylethenes are among the most

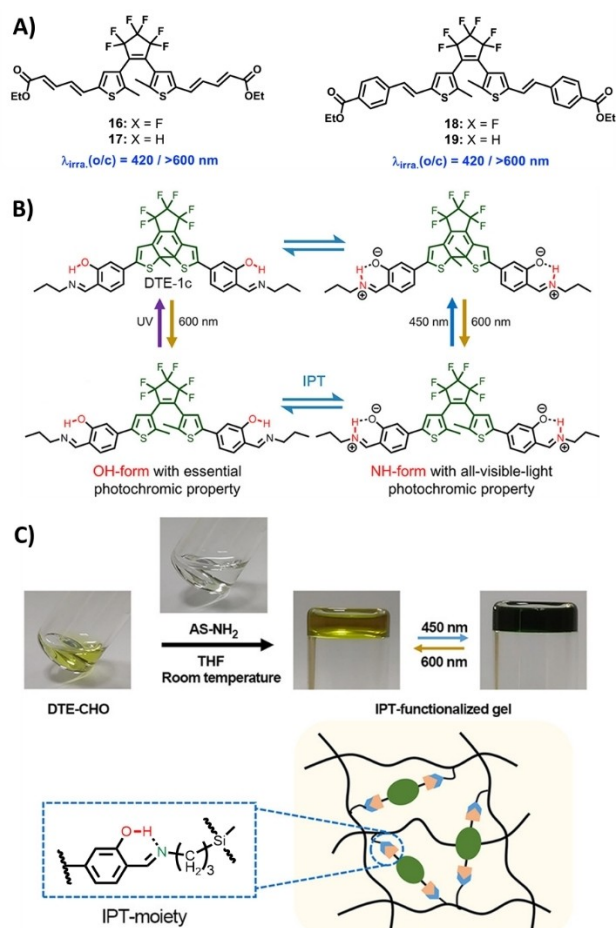


**Figure 5.** A) Modulating hydrogel contraction or expansion by incorporation of different spiropyran moieties within hydrogel networks; reproduced with permission from Ref. [26a] Copyright (2020) American Chemical Society. B) Representative chemical structures and spectra (in acetonitrile) of red-shifted spiroyrans by incorporation of a conjugated cationic fragment in the 2H-chromene moiety; reproduced with permission from Ref. [29b] Copyright (2020) Elsevier.

studied photoswitches for such applications due to their thermal stability, fast response, and excellent fatigue resistance.<sup>[30]</sup> Significant efforts have been made to develop fully visible light activated diarylethenes for practical applications. The main chemical approach to red-shift the photo-reactivity of diarylethenes involves extending the  $\pi$ -conjugation, reducing the HOMO-LUMO energy gap of the open form for visible light triggered reversion (Figure 6A).<sup>[31]</sup> However, the preparation of such molecules is demanding, featuring multiple synthesis steps, and the resultant chromophores often have poor photochromic performance. Consequently, their applications in crosslinked polymer networks are limited. More recently, the team of Zhu incorporated intramolecular proton transfer (IPT) moieties to diarylethene core, enabling red-shifting of the photoreactivity while retaining the excellent photoswitching efficiency.<sup>[32]</sup> Notably, the IPT moieties contain an imine group formed by amine-aldehyde coupling reaction, and can be used to fabricate polymer networks with in situ incorporation of visible light-responsive diarylethene (Figure 6B).<sup>[32]</sup> Such a photochemical platform shows key potential for addressing multi-functional all-visible-light-modulated materials.

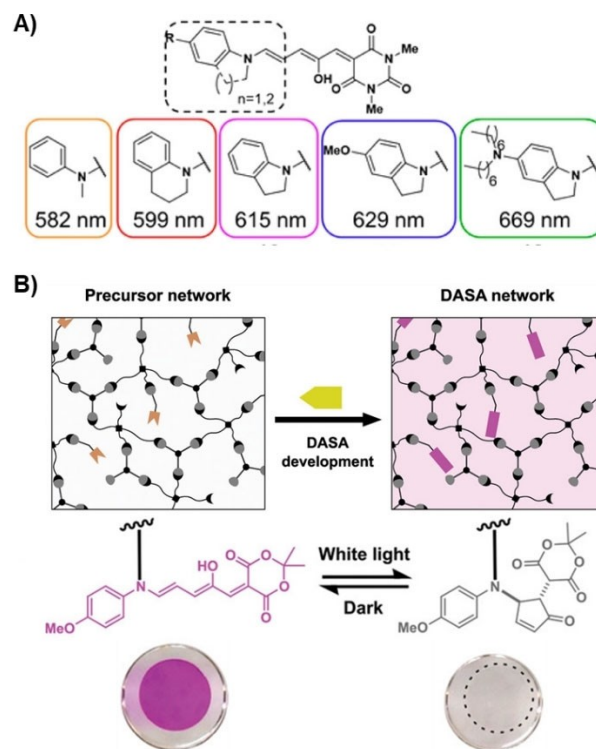
### Donor-acceptor Stenhouse adduct (DASA)

DASAs are a nascent class of negative photochromic photoswitches, reported in 2014 by the team of Read de Alaniz.<sup>[33]</sup> DASAs have absorbance bands in the visible region, and they



**Figure 6.** A) Representative chemical structures of red-shifted diarylethenes'  $\pi$ -conjugation at the 5,5'-positions; reproduced with permission from Ref. [31b] Copyright (2020) Elsevier. B) Fully visible light photochromism of diarylethene via IPT, and C) formation of a photoresponsive crosslinked structure containing the red-shifted diarylethene (AS-NH<sub>2</sub>: amino-functionalised siloxane polymer). Reproduced with permission from Ref. [32] Copyright (2019) American Chemical Society.

can be efficiently synthesised from the inexpensive (bio-based) feedstock furfural. Under visible light irradiation, the strongly coloured conjugated triene form is rapidly photobleached to the colourless cyclopentenone (Figure 7).<sup>[33]</sup> They also display a significant change in polarity, dipole moment, and geometry upon photoswitching. Such structural property changes enable a plethora of applications in drug release, chemosensing and catalyst recycling.<sup>[34]</sup> A major limitation of these photoswitches is the low thermal stability in protic solvents, such as water and alcohol, in which the open form rapidly converts into the closed form and loses photoresponsiveness. DASAs with significantly red-shifted reactivity, such as the recently introduced 2<sup>nd</sup> and 3<sup>rd</sup> generations,<sup>[35]</sup> (Figure 7A) can be activated by far red and NIR light. Some of these molecules have been covalently incorporated into polymer networks by post-modification of polymer chains, affording 3D photochromic networks whose colour can be tuned on demand by white light (Figure 7B).<sup>[36]</sup>



**Figure 7.** A) Representative structures of red-shifted DASAs with absorbance extending well into the NIR region; reproduced with permission from Ref. [34b] Copyright (2019) American Chemical Society. B) Design of a DASA-incorporated polymer network and schematic depiction of the photoisomerization, enabling the change in material colour.<sup>[35]</sup>

Given the rapid development of new DASA compounds, this class of photoswitches is expected to compete with and complement well with existing prevalent photoswitches such as azobenzenes, spiropyran, and diarylethenes for the development of novel photodynamic networks.

## The Next Frontiers of Photodynamic Polymer Networks

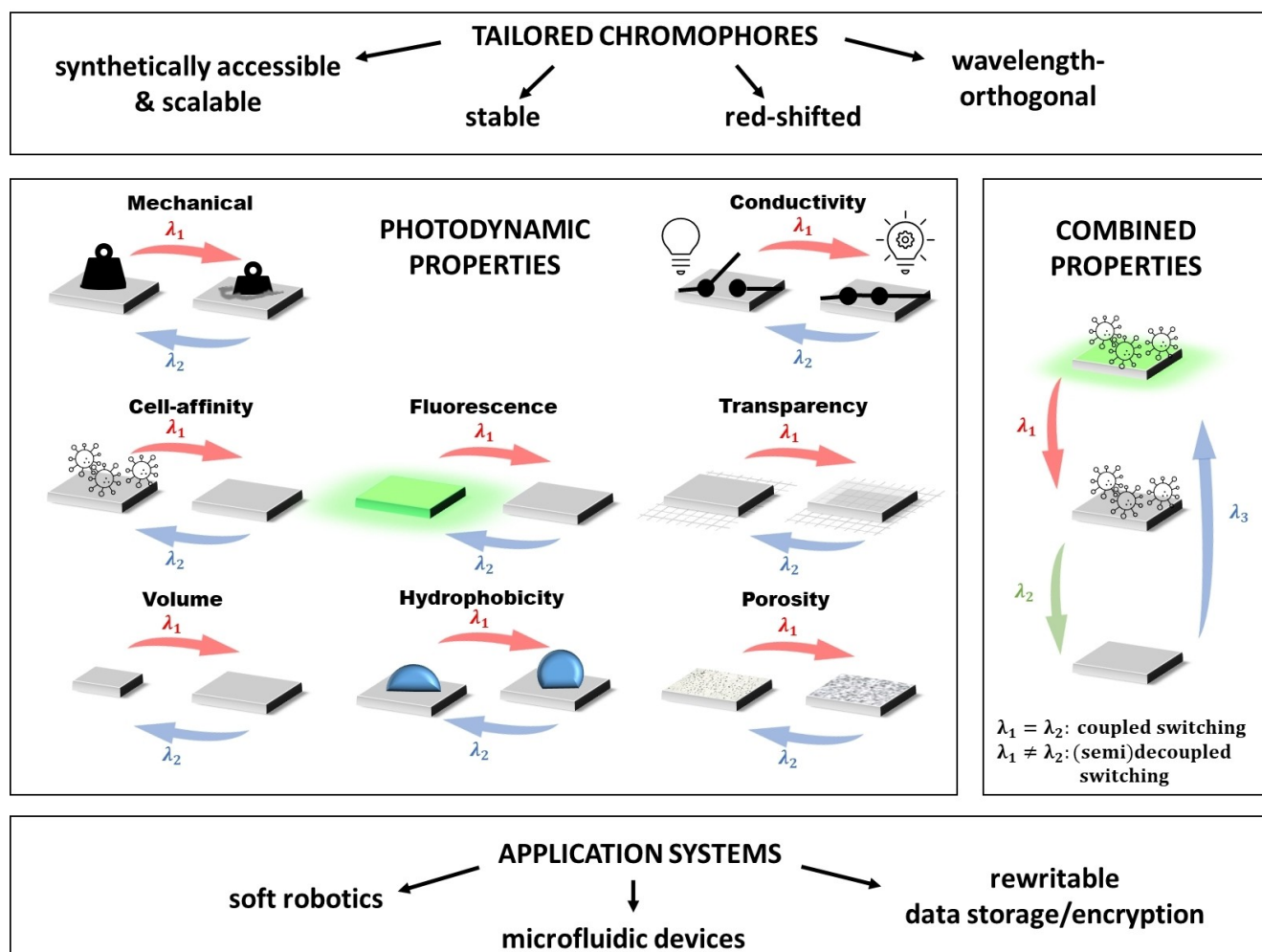
The field is now at the cusp of making advances that previously seemed unattainable yet have come within reach in the next decade or so: Here, we explore the future, speculate on what network properties might be adaptable by light and discuss what is required to achieve these goals.

### Expanding the scope of light-programmable properties

While some adaptations are currently attainable in networks to a certain degree (e.g., change in mechanical or optical behavior, volume, fluorescence, polarity), many more are waiting to be unlocked, e.g., tuning of porosity, or even more exotic properties like conductivity or magnetism, which may all be applied in advanced applications such as soft robotics or microfluidics

(Figure 8). Looking beyond the inherent material properties and towards the functions these properties can fulfill, there seem to be sheer endless possibilities. For example, optical property switching includes transparency and color of a material, porosity influences its permeability, degradability, and drug-releasing ability. Hydrophobicity may further influence drug-release, cell-affinity or adhesiveness. Here it should be mentioned that we will subsequently describe property changes as switching between two states. While this is an appropriate description for most current systems, property changes may also occur more fluently/blurred, which can be desirable depending on the application. However diverse these photodynamic properties may seem, they all have several challenges in common (Figure 8).<sup>[37]</sup> Most importantly, the chromophores for such systems must be easily accessible regarding their synthesis, scalability, and cost efficiency. Furthermore, they must exhibit sufficient stability during network formation despite ideally red-shifted photoreactivity. Red-shifting not only holds synthetic challenges, yet may also be problematic for

some applications where ambient light interferes with material stability. This is of course dependent on the light intensity necessary for system activation. An additional stimulus, such as pH or temperature, may be used in conjunction with light to provide a “safety switch” when the visible light-responsive materials are exposed to natural light sources, such as sunlight. While the issue of red-shifting photochemical reactions has become the center of attention already, availability and applicability in materials are still sometimes disregarded in the design stage of new chromophores even though the implementation of chromophores in polymer networks impacts their macroscopic properties such as strain at break, modulus, or glass transition temperature, all of which influence the application and/or the photodynamic reaction. From a systemic point of view, the photochemical reaction is affected by the more restricted solid state, particularly when the chromophores are included covalently in the network. Spatial effects manifest themselves twofold: firstly, via a photostationary state that is favored towards the non-bonded form<sup>[38]</sup> and secondly via



**Figure 8.** Several key attributes of currently accessible chromophores have been identified, which are required to push the current boundaries of the field. This will expand the range of photodynamic properties on the one hand and enable more flexible photo-switching in networks to include more than one property on the other hand. As a result, increased photodynamic property variety and clever combinations thereof pave the way towards new application systems.



hindered rotational freedom of photoswitches.<sup>[39]</sup> The large discrepancy between the number of reports for molecular photo-switching studies in solution versus in solid-state materials is a clear manifestation of the limits imposed by steric confinements. Within the realm of solid-state systems itself, the number of reported light-directed applications, especially red-shifted ones, decreases with increasing steric confinement, from surfaces to solid molecular aggregates such as liquid crystals or photo switches to polymeric materials with sidechain incorporated chromophores to polymeric networks, where the chromophores contribute to the formation of covalent networks.<sup>[40]</sup> In addition to the issue of steric confinement, sufficient light penetration of networks constitutes a challenge, in biological settings particularly at wavelengths below 400 nm.

Considering these observations, it is remarkable how many light-tunable properties have been reported already. Mechanical changes of networks upon irradiation have been established early on, with emphasis on irreversible and reversible degradation and crosslinking processes. As mechanical changes are arguably the most established photodynamic property, most red-shifted and/or network-forming chromophores are also reported for this purpose.<sup>[11c,12]</sup> Furthermore, light-controlled fluorescence has become a valuable tool with most applications utilizing covalently incorporated chromophores.<sup>[41]</sup> Due to their importance for optical data storage, photochromic polymer networks have also come a long way already.<sup>[41]</sup> While further properties have been proven to be light-tunable, it must be mentioned at this point that these examples are still scarce, particularly in combination with red-shifted chromophores. For example, molecular concepts have already explored volume changes and even porosity tuning via isomer switching.

However, only few such molecules have been translated into applications as polymeric networks, mostly spiropyrans.<sup>[26a,c,27]</sup> Tuning hydrophobicity, which has also been exploited to manipulate cell behaviour, has been shown in hydrogels.<sup>[11c,42]</sup> Forming and cleaving conjugated networks and thus switching between the conducting and insulating state via photochemical reactions is particularly challenging due to the inherent switching of absorptivity for these two states but would be highly rewarding with a range of applications in microelectronics. Extensive efforts in this regard have been made in molecular layers of photoswitches, polymeric systems doped with molecular photoswitches, and side-chain incorporated photoswitches in thin polymer films.<sup>[14,43]</sup> However, transitioning of these concepts into covalent networks remains an unmet challenge. To the best of our knowledge, switching organic matter with light between magnetic states has progressed even less than conductance switching. Some examples exist on the molecular level but not for materials.<sup>[44]</sup>

### Combining multiple light-programmable properties

On the one hand, many examples exist for multi-stimuli responsive networks incorporating more than one programmable property in materials. Stimuli include for example pH, solvent, mechanical force, that typically do not provide tempo-

spatial control and/or non-invasive triggers. Light-triggered responsive networks, on the other hand, offer exclusive potential for improved non-invasive spatio-temporal and even remote control, particularly with respect to reversibility. This is especially desirable for generating materials capable of complex responses as it is for example necessary for soft robotics or rewritable data storage. However, examples for the implementation of several programmable properties solely stimulated by light are scarce. While we are able to precisely map photochemical reactivity,<sup>[5]</sup> the number of truly wavelength-orthogonal systems is still limited, thus requiring further discovery and in-depth investigation of wavelength-orthogonal photochemical systems. These will pave the path towards more complex applications such as soft robotics, programmable microfluidic devices, and rewritable data storage/encryption. Integration of several independently reversible photoresponsive properties into one material currently exceeds the state of the art as two exclusive wavelength ranges per reversible photoreaction are necessary for independent control over these reactions and only a few truly red-shifted reactions are available.

A first step towards this goal is simultaneous switching of two properties. For example, reversible mechanical property changes can be combined with on/off switching of fluorescence to report the property change by combining two reversible photoreactions, which utilize the same wavelengths for the forward and reverse reaction. While this has been realized to some extent with only one chromophore,<sup>[45]</sup> systems with the same functionality containing two chromophores are yet to be established to the best of our knowledge. Another possibility how multi-responsive behavior based solely on light stimulation has already been implemented, is by using the light-induced change of one property as a trigger for a subsequent change of another property. For example, a strain-induced chromophore has been switched by light-dependent mechanical changes of a material.<sup>[46]</sup>

First approaches towards semi-independent property changes, where the photoreactions of two chromophores are independent from each other, whereas their reverse reactions occur at the same wavelength or vice versa, have been explored. For example, spiropyran and diarylethene have been utilized in radically prepared networks, which can exhibit three states, red, green, or non-fluorescent.<sup>[47]</sup> While here only one property type, i.e., color, is addressed, a photochromic luminescent liquid crystal elastomer actuator using covalently linked tetraphenylethene for fluorescence and spiropyran moieties for shape-morphing has been realized, where two different properties are switched semi-independently.<sup>[48]</sup>

Combining two different wavelength-orthogonal photochemical reactivities is particularly exciting compared to the use of other external stimuli as it allows the creation of more complex spatial and temporal patterns such as oscillatory isomerization or logic “and”/“or” switches, which could be utilized in soft robotics. Most investigations of such principles have been conducted in small molecules.<sup>[49]</sup> In rare cases basic applications of this concept in linear polymers or networks have also been studied.<sup>[50]</sup> Generally, these reports provide a proof of concept but do not look further into cyclability of the systems.

However, cyclability may be endangered through side reactions, especially since these systems usually utilize UV-induced photo-reactions, which are prone to side reactions. Furthermore, such multi-responsive systems are almost exclusively based on isomerization reactions and to the best of our knowledge no bond breaking or forming reactions occur in such systems yet. Above all, several concepts have only been proven on the small molecule level or in supramolecular materials. Therefore, bridging the gap between molecular and network studies further by translating the most promising molecular examples into network settings and identifying new challenges due to the new environment is the next step towards materials with multiple reversible light-directed properties with high cyclability. This could be pursued both theoretically and experimentally.

### Wavelength-dependent network formation

Up to this point, the discussion revolved around light-switching of properties of an existing network. Creating gradually changing network properties during light-induced network fabrication, however, is largely unexplored. Additive manufacturing (AM) offers the unique possibility to form three-dimensional structures based on orthogonal light exposure of photoresists. This could be exploited to print multiple materials with different colors of light and generate uniquely complex gradient materials. Such a process requires pioneering work on various levels. Firstly, several unique features are necessary for a 3D printer capable of this task, which have not been addressed for these machines so far. Two paths for light of different wavelengths must be implemented, which aim at the same volume with high spatial and temporal precision, intensity, and beam quality. Furthermore, switching between two light sources must be possible under these circumstances. Finally, a preferably large range of wavelengths should be accessible with the setup. Secondly, stringent requirements also apply to photoresists for this purpose. Obviously two photoresists must be available, which build up networks upon irradiation, implying that two photodynamic reactions, which are wavelength-orthogonal to each other, must be employed as the main crosslinking reaction. At the same time standard pre-conditional attributes for the printability of a photoresist apply, such as sufficient solubility (or sufficiently low viscosity) and reactivity. The system would also require sufficient compatibility of the photoresists in the printing formulation to prevent photoresist segregation, which would trigger inhomogeneous curing and light scattering. Evidently all these attributes rely again on the careful tailoring of the chromophores as described above. In addition, clever linking strategies are necessary to make larger quantities of sufficiently soluble multifunctional monomers.

While photocurable interpenetrating networks are an early example of dual color network curing,<sup>[51]</sup> the attainable spatial resolution between the two curing reactions is non-existent or realized by selective degradation or post-modification rather than orthogonal curing in most cases.<sup>[52]</sup> Further progress

towards this ultimate goal has been achieved through the introduction of solution mask liquid lithography (SMaLL), which utilizes semi-orthogonal chemistry to realize a continuous process, which produces non-layered objects.<sup>[53]</sup> A similar approach is multimaterial and spatial-control DLP-AM (MASC DLP-AM), which semi-orthogonally cures radical and cationic networks through the use of semi-orthogonal photoinitiators for the respective systems.<sup>[54]</sup> However, these processes enabled curing of both, the cationic and radical resin, under UV irradiation, resulting in IPNs, or radical-only curing upon irradiation in the vis range. While photoinitiated chain growth polymerizations have seemingly exhausted their capability for wavelength-orthogonal curing, the individual curing of each network remains, to the best of our knowledge, unexplored.<sup>[55]</sup> Furthermore, the formed bonds are not dynamic post-printing. Utilization of light-stimulated reversible ligation reactions could instead lead the way towards dynamic material behavior post-printing. In combination with multiple light stimulated materials, the printing process could potentially even be decoupled from other light-responsive properties.

In summary, the advancement of existing wavelength-orthogonal photodynamic networks and tapping the full potential of this largely unexplored concept depend on three general aspects, which must be optimized further. (i) Most photoreactions still lack efficiency in cyclic reversibility, particularly if they rely on short wavelength, high intensity conditions. (ii) While good progress has been made to shift forward reactions towards longer wavelengths, their reverse reactions usually still rely on UV light. Extending the scope of red-shifted reactions, including their reverse reactions – while maintaining sufficient band separation from other light-controlled reactions – is therefore key. (iii) One particularly important aspect from the material design perspective is the development of synthetically readily accessible, sufficiently stable, and small chromophores, which interfere only marginally with the original design of material properties.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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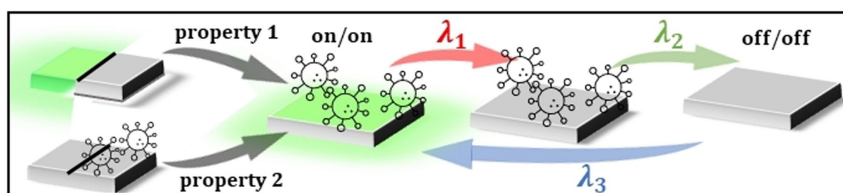
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## CONCEPT



**Photodynamic properties** allow materials to switch between two or more states, for example, fluorescence on/off, biocidal/cell-attracting. Implementation of such properties into materials requires the insertion of carefully tailored chromophores into polymer networks. The current

concept article highlights the state-of-the-art for current, red-shifted photodynamic networks, explores their limitations, and foreshadows the potential of future photodynamic networks once these limitations are overcome.

*Dr. V. X. Truong\*, Dr. K. Ehrmann, M. Seifermann, Prof. Dr. P. A. Levkin\*, Prof. Dr. C. Barner-Kowollik\*, Selected by the Editorial Office for our Showcase of outstanding Review-type articles .*

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**Wavelength Orthogonal Photodynamic Networks**

