Macromolecular Chemistry and Physics
www.mcp-journal.de

Synergistic, Orthogonal, and Antagonistic Photochemistry for Light-Induced 3D Printing

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Dedicated to Prof. Brigitte Voit on the occasion of her 60th birthday

3D printing techniques are often based on light-induced chemical reactions, driven by the fascinating and powerful possibilities to control light in space and time. To date, these approaches are usually restricted to a single color of light, which does not do justice to light as an entire spectrum of distinct wavelengths. It is possible to further tap into the vast potential of light-induced 3D printing by introducing a second color of light. While the complexity of photochemical interactions in two-color systems is greatly increased, it concomitantly allows for enhanced control over manufacturing speed and resolution. In general, three types of two-color interactions can be distinguished, i.e., synergistic, orthogonal, and antagonistic. In recent years, intriguing printing techniques with superior potential for the fabrication of 3D structures are emerging that require two colors of light. Their future development potential is vast yet needs to be critically underpinned by an advance in complex tunable photochemical reaction systems. The current perspective will thus explore the potential for using synergistic, orthogonal, and antagonistic photochemistries in 3D printing.

1. Introduction

Light plays a key role in the development and continuation of life on earth.[1] For example, photosynthesis continuously fixates the carbon dioxide in the air into organic matter, which in turn enables life and feeds the world.[2] Inspired by the outstanding and singular significance in nature, the chemistry of light has received great attention in the macromolecular sciences as it offers a high level of potential and opportunities, especially for the design and manipulation of polymeric materials. One of the most critical assets of photochemistry is enabling a straightforward and precise control over where and when light is applied as a stimulus, i.e., its spatiotemporal control.[3–5] Light in general is environmentally friendly and innocuous for living organisms, making it a valuable tool for biological applications.[3,6] Moreover, the option to work with distinct wavelengths of light introduces a new dimension of control in addition to space and time, thus offering a myriad of new and exciting possibilities.[4] These possibilities are based on the fact that disparate colors of light are capable of selectively inducing different responses in a system, i.e., activation or deactivation of specific chromophores.[4] In order to fully exploit the advantages of light as a spectrum, it is of utmost importance that these responses can be triggered independently of each other. This

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DOI: 10.1002/macp.202200318

behavior is known as λ-orthogonality and has been extensively explored and reviewed in the recent years.[4,7–10] Especially in the field of light-induced 3D printing, advanced photoresists and printing techniques revolve around the exploitation of two distinct colors of light.[11–14]

The current perspective discusses and highlights contemporary approaches for two-color 3D printing, which are based on three different types of light-interactions with a photoresist, i.e., synergistic, orthogonal, and antagonistic. In a synergistic system, both colors of light need to be present at the same place and at the same time in order for a covalent bond to form and enable a printing process. Such systems allow for the employment of techniques for very fast and precise printing.[12,14] In orthogonal systems, two disparate reactions are triggered independently by the different colors of light, making it possible to print diverse material properties from a single photoresist.[15] Finally, in antagonistic systems, one color activates the printing, while the other one has a deactivating function. This behavior can be exploited, inspired by stimulated emission depletion (STED) microscopy, to allow for printing on the micro- and nanoscale, well below the diffraction limit.[13,16,17]

Recent publications[11–16] show that new possibilities and benefits of 3D printing with two colors of light are already vast and intriguing, but what if printing became even more colorful?

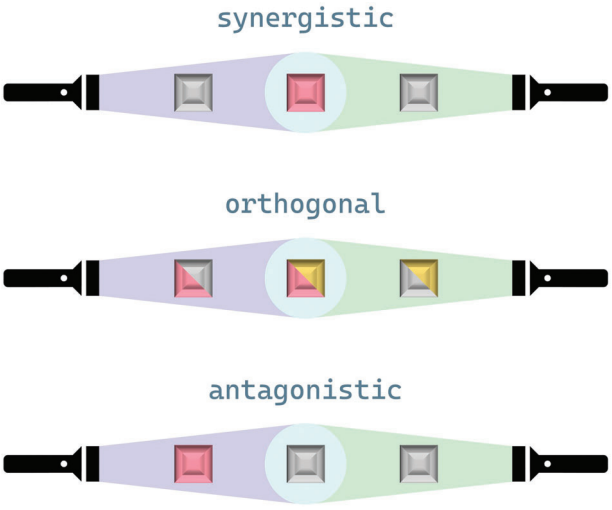

Figure 1. Schematic illustration of different two-color systems, i.e., synergistic (top), orthogonal (middle), and antagonistic (bottom).

2. Printing with Two Colors of Light

3D printing has been established as an extremely valuable tool for the tailored fabrication of structures, predominately in the automotive industry[18] as well as in the fields of electronics[19] and healthcare.[20] In particular, light-induced additive manufacturing has received special attention and various printing techniques (e.g., stereolithography, digital light processing, and two-photon laser printing [also known as direct laser writing]) have been developed for fabrication of structures on the macro-, micro- and even to the nano-scale.[21] These approaches are based on the photochemical crosslinking of a photoresist by accurately applying a single source of light with a narrow wavelength distribution, i.e., a laser or diode.[22]

The first mentions of two-color 3D printing go back to a 1974 column by Jones in *New Scientist*[23] and a 1977 patent by Swainson.[24] However, they did not make any particular suggestions as to the chemical realization. In recent years, two-color 3D printing, which involves adding a second light source of a different wavelength, has received increasing attention.[11,12,15,16] In this section, the different light-interactions depicted in **Figure 1**, i.e., synergistic, orthogonal and antagonistic, will be explained in detail with the help of current breakthroughs in the field. Furthermore, comparisons with the state-of-the-art two-photon absorption approach for 3D nanoprinting will be made to elucidate and highlight the advantages of introducing a second color. To enhance the reading experience, a glossary containing the most important terminology related to the current perspective has been compiled in Table S1, Supporting Information.

2.1. Synergistic

The concept of synergy implies that the combination of two or more factors results in something greater than the sum of their individual effects.[25] Teamwork is a great example, aiming to gather the ideas and strengths of different people in order to be more innovative and increase efficiency.[25] Similarly, additive manufacturing with two instead of only a single color of light as envisioned by Jones and Swainson (see above) provides the opportunity of synergistic interactions that have been harnessed for access to completely new and superior printing techniques.[11,12]

In 2019 Wegener and co-workers[11] introduced light-sheet printing as a novel concept for fast and precise 3D printing on the microscale. This approach was inspired by light-sheet optical microscopy and is based on synergistic interactions of photoresist and two disparate wavelengths of light, where the printing process is only initiated at the intersection of both beam paths. This premise is exploited by focusing a thin sheet of light through the photoresist and projecting an image of another wavelength onto this sheet (**Figure 2**A). Scanning the sheet across the photoresist while varying the projected image enables the fabrication of intricate 3D structures in a short amount of time. Compared to two-photon printing processes, which take place in an extremely small part of the laser focus (termed the voxel) with commercial state-of-the-art minimum feature sizes of down to 100 nm at writing speeds of up to 10 cm s^{-1} (nearly 10^6 voxels s^{-1}),[17] printing sheetwise has the potential to be orders of magnitude faster, while still maintaining accuracy on the microscale. Moreover, instead of an expensive and space consuming femtosecond laser, much more economical and smaller continuous-wave lasers or light-emitting diodes can be employed.[11]

While the theoretical benefits and practical opportunities offered by light-sheet printing are apparent, it is important to highlight the second key element besides the optical set-up, an "AND-photoresist" (synergistic).[11] Designing such a photoresist represents a formidable challenge since several very intricate properties have to be guaranteed at once. A crosslinking reaction, i, covalent bond formation, must only occur when two distinct colors of light meet in a certain volume element in the photoresist. Precise control over the printing process requires the chemical responses triggered by each color to proceed in a completely λ-orthogonal

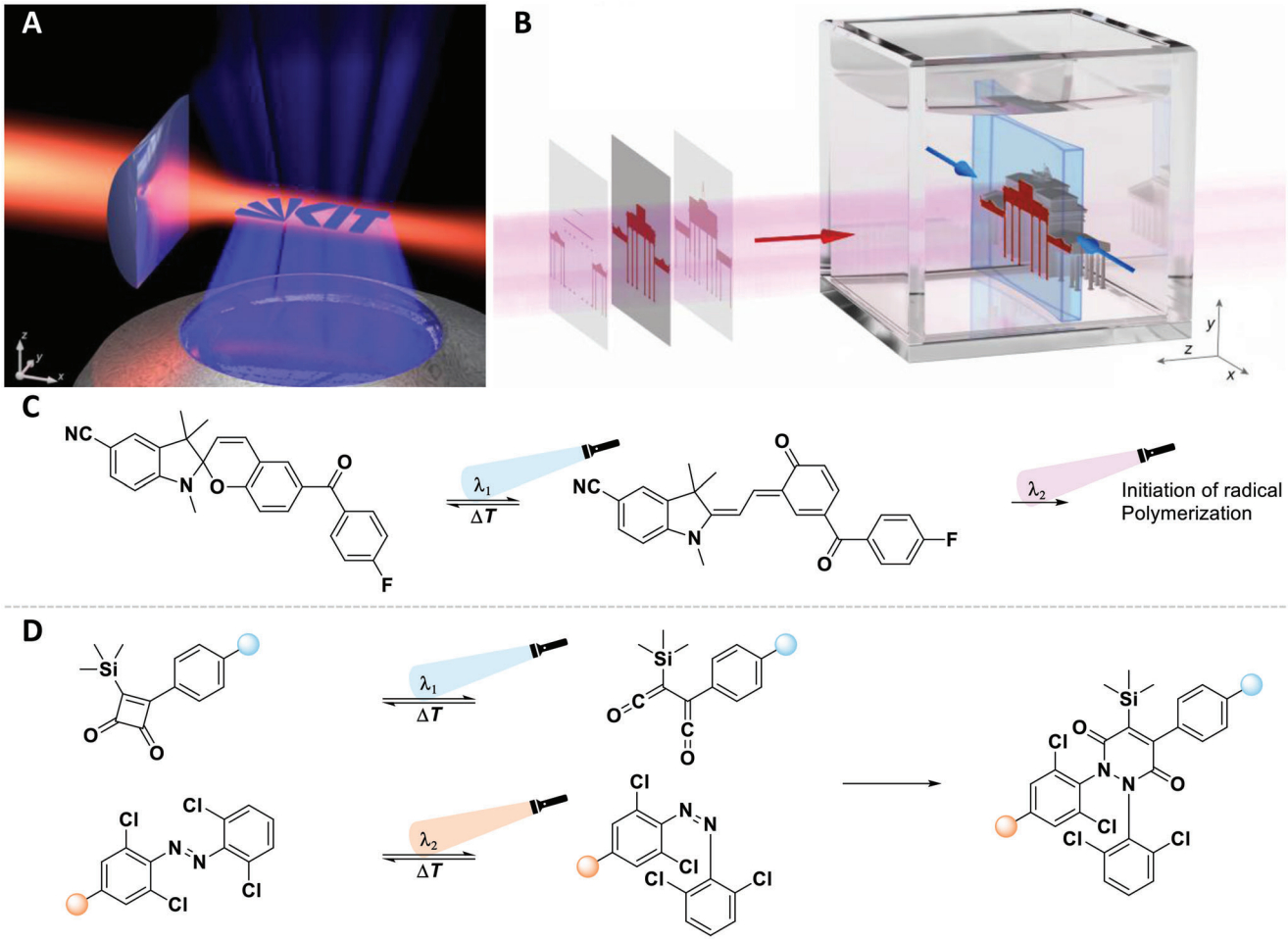

Figure 2. A) Model illustration of light-sheet printing, where an image of one wavelength (violet–blue) is projected into a sheet of light of another wavelength (red–orange). Only at the intersections of both wavelengths a printing process is initiated. Reproduced with the author's permission.[11] B) Rendered illustration of the printing zone in xolography. Reproduced with permission.[12] Copyright 2020, Springer Nature. C) Chemical structures and mechanism for the two-color activation of a spiropyran photoswitch with an integrated benzophenone photoinitiator in xolography.[12] D) Synergistic two-color light activated formation of covalent bonds between a diketene (top) and a *cis*-azobenzene (bottom) upon exposure to light of 385 and 625 nm.[14]

manner. Furthermore, the wavelength-dependent changes in the system need to be fully reversible in a short time in order to thoroughly harness the virtues of spatiotemporal control. The only irreversible change in the photoresist should be an efficient two-color activated crosslinking, as recently demonstrated by our team.[14]

The first two-color 3D printing advance based on synergistic photochemistry was reported by Hecht and colleagues in 2020[12] as a linear volumetric printing process termed xolography. The optical set-up is similar to light-sheet printing with a sheet of UV light (375 nm) onto which an image in the range of visible light (585 nm) is projected as depicted in Figure 2B. The photoresist is based on the monomer pentaerythritol triacrylate, which is cross-linked by the two-step activation of a dual-color photoinitiator consisting of a spiropyran photoswitch with an integrated benzophenone photoinitiator. UV light induces the switching of spiropyran to merocyanine, which is subsequently able to absorb visible light and activate the benzophenone unit, leading to radical generation and thus starting a printing process (Figure 2C).

With these underlying principles, xolography has been demonstrated to fabricate objects with complex structural features, while displaying high resolution and printing speed (Hecht and colleagues estimate a voxel size of 37.5 µm,[12] leading to a printing rate of 1.8×10^6 voxels s^{-1}, whereas we estimate a voxel size of 90 µm, leading to a printing rate of 8.6×10^4 voxels s^{-1}). Nevertheless, the responses to the different wavelengths of light are not completely λ-orthogonal, because merocyanine also absorbs in the UV range which then results in uncontrolled competing initiation.[12,14]

Earlier this year, a new approach for a synergistic photoresist, based on the completely λ-orthogonal activation of two different photoswitches has been reported by us.[14] Only in their activated states can these compounds undergo an efficient covalent bond forming reaction with each other, which was demonstrated to irreversibly crosslink a polymer network. This system is based on the *trans* to *cis* isomerization of an azobenzene at 385 nm and the reversible formation of a diketene at 600 nm, followed by a [4 + 2] cycloaddition of the excited species (Figure 2D).

Furthermore, activation of the photoswitches is completely reversible, which is critical for enhancing the control and helps to avoid competing side reactions when printing. However, the reversibility of the photoactivated diketene is only rapid at elevated temperatures around 70 °C. Thus, the advantage of improved control due to reversibility cannot be harnessed during the printing process, which limits potential applications, e.g., light-sheet printing is not feasible.[14]

It becomes apparent that even though the research on two-color printing started a few years back and is still in its infancy, several approaches based on synergistic photochemistry have already been reported[11,12,14] and will surely motivate and inspire subsequent research on the topic.

2.2. Orthogonal

The concept of orthogonality in a chemical context was first introduced by Merrifield and Barany in 1977,[26] when they reported an innovative approach for peptide synthesis. Originally, the term was used to describe disparate protecting groups that were removed one by one by successively employing different reaction conditions. Today, the general idea of orthogonality describes the ability to manipulate particular changes in a chemical system independently of each other by controlling the process parameters. In this regard, the potential within photochemistry is enormous, since wavelength as a parameter entails almost unlimited possibilities with the entire spectrum of light.[4]

The selective activation of different chromophores at different wavelengths of light is termed λ-orthogonality. Initially, it is important to define the two different types of λ-orthogonal behavior, i.e., sequence-selective and sequence-independent. In the first case, λ-orthogonality is conditional on the color-sequence of irradiation, which typically progresses from longer to shorter wavelengths, as most chromophores absorb light in the high energy UV region and can thus not be excited in a discrete manner.[27] Since orthogonality is only guaranteed under certain conditions, sequence-selective λ-orthogonality will be referred to as λ-selectivity herein. In the second case, individual photoactivation of different chromophores is completely independent from the sequence of colors applied. In the following, λ-orthogonality will be referring to this unrestricted and ideal type of orthogonal behavior.[4,8,9,28,29]

The key benefit of λ-orthogonality to selectively address different chromophores, depending on the wavelength of light, raises the potential for multimaterial 3D printing from one photoresist. In other words, only a single photoresist cartridge in the printer would suffice to manufacture complex multimaterial structures, e.g., by introducing soft and hard elements, or electrically conducting and insulating properties, respectively.[8] The development of corresponding multicomponent photoresists would drastically enhance the versatility of 3D printing in a straightforward manner and is an important step for the feasibility and establishment of 3D printing in our daily lives.

Design and printing of the first photoresist based on sequence-independent λ-orthogonal photochemistry was reported by us in 2019.[15] The system is based on discrete dimerization reactions of a photocaged diene generated from an *o*-methyl benzaldehyde (*o*-MBA) and a styrylpyrene (StyP), triggered by UV light (330 nm) and visible light irradiation (435 nm), respectively (**Figure 3**). Both chromophores are attached to separate poly(methyl methacrylate) backbones. Solely by adjusting the applied wavelength, two disparate materials were successfully printed from a single photoresist and the first platform technique for λ-orthogonal photoresists was established.[15]

However, the design of photoresists for the λ-orthogonal 3D printing of complex multimaterial structures is definitely a formidable challenge. Nonetheless, the potential and benefits of employing a single starting mixture to manufacture an array of diverse and complex materials will allow to drastically expand the scope of applications for 3D printing.

2.3. Antagonistic

Some of the most important movements of the human arm are regulated by the antagonistic pair of biceps and triceps. Contrary actions, i.e., flexing and stretching, are performed by these muscles and only the coordinated combination of both allows for very precise and controlled motions.[30] The same principle applies to antagonistic interactions in photochemistry, where two colors of light separately trigger either one of the opposing processes of activation or deactivation of a chromophore. In the field of 3D printing, this precision-enhancing counterbalance has been exploited to fabricate objects with an extremely high resolution.[16,31]

Additive manufacturing of complex structures on the micro- and nano-scale offers a multitude of possible applications, e.g., in the fields of photonics, biophysics, and optofluidics.[32] Currently, precise printing with nanometer resolution can be realized by the state-of-the-art electron-beam lithography, however this technique only allows for planar patterning (2D and 2.5D structures) and is also associated with high cost due to expensive equipment.[33,34] In recent years, multiphoton absorption polymerization lithography was established as a valuable tool for the realization of 3D structures with transverse feature sizes to below 100 nm.[32] Typically, a near-infrared femtosecond laser is employed and focused on an extremely small volume in the photoresist to induce a crosslinking reaction that is only triggered by the simultaneous absorption of two photons at once. As a result, the reaction becomes extremely improbable and only leads to solidification of the photoresist directly in the laser focus due to an extremely high photon density. Accordingly, the volume of the smallest printing element (voxel) is kept at a minimum and allows for precise printing on the micro- and nano-scale.[17] Nevertheless, infinitely downsizing the laser focus to achieve arbitrary small feature sizes is limited by the laws of optical diffraction. The diffraction limit is proportional to the wavelength of the laser light and can be decreased by employing lower wavelengths.[35] However, since multiphoton absorption polymerization relies on the improbable coinciding absorption of multiple low energy photons, introducing photons of higher energy would result in a one-photon absorption process, thus having an adverse effect and sharply decreasing the resolution, instead of the desired increase.[17,35]

In 2014, Stefan Hell was awarded the Nobel Prize in Chemistry for the development of STED microscopy, which enables high resolution imaging below the diffraction limit, by the antagonistic interactions of two different colors of light.[36] This

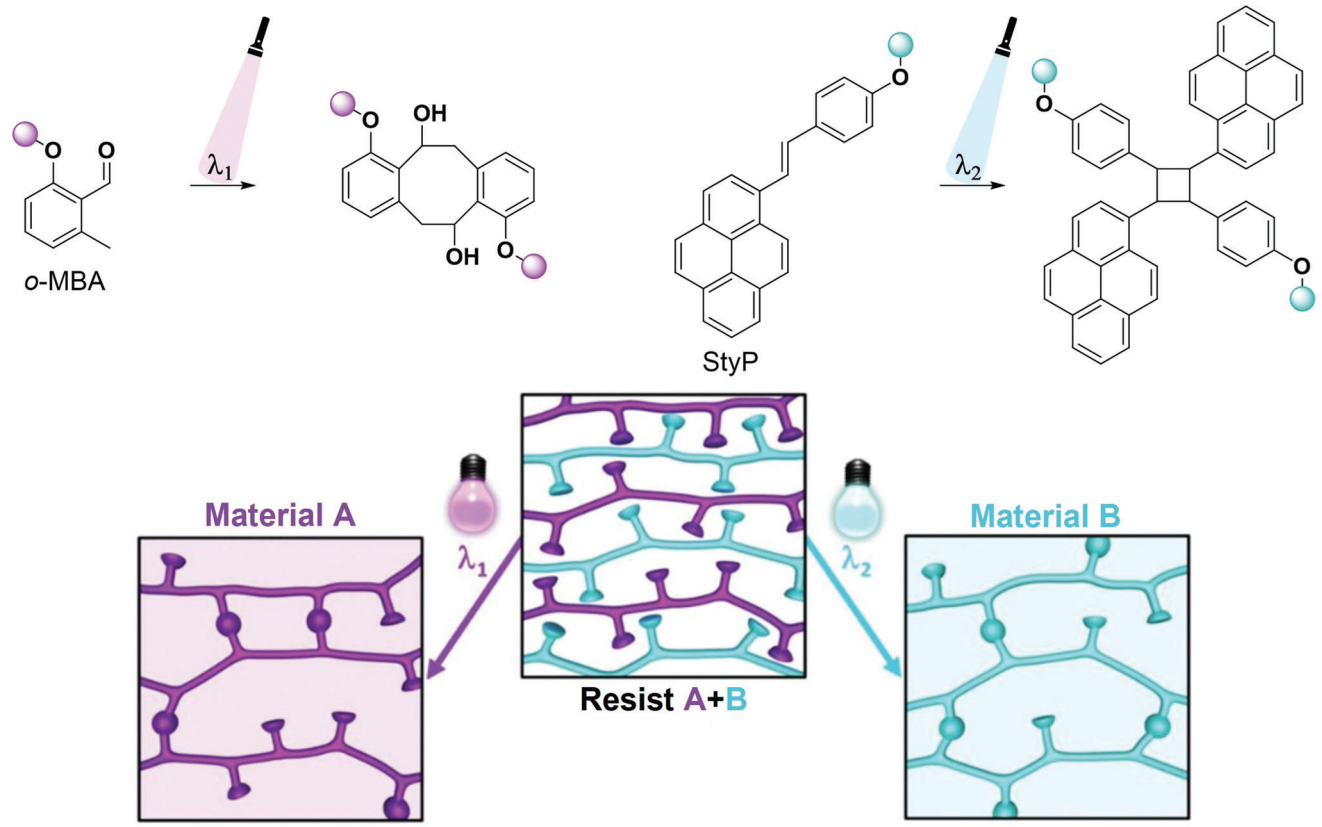

Figure 3. General concept of λ-orthogonal 3D printing with a single multimaterial photoresist. Material A is cross-linked upon exposure to wavelength λ_1 (330 nm, *o*–MBA-dimerization) and material B with wavelength λ_2 (435 nm, StyP-dimerization). Adapted with permission.[15] Copyright 2019, Wiley-VCH GmbH.

inspired a very promising approach for high resolution two-color 3D printing of a tailored photoresist. The first wavelength excites a chromophore, which in turn induces a crosslinking reaction, whereas the second wavelength has a depleting function and deactivates the excited chromophore by stimulated emission, hence suppressing the crosslinking. The general setup is typically based on two-photon lithography to trigger a printing process, with the addition of a second, deactivating laser beam that is focused around the first one, e, in a donut shape. Consequently, the effective voxel size can be scaled down by increasing the intensity of the deactivating light. In this manner, the diffraction limit has been broken.[13,16,32,34,35,37]

In 2010, Wegener and co-workers[13] reported the design of a novel photoresist, consisting of the monomer pentaerythritol triacrylate and isopropyl thioxanthone (ITX) as photoinitiator (**Figure 4**A). Radical crosslinking of the photoresist is promoted by two-photon absorption at 810 nm. Interestingly, by additionally applying laser light in the green range (532 nm), stimulated emission of the exited ITX is favored over the initiation of radical polymerization. For minimization of the voxel size, the depleting wavelength is focused on a donut shaped mode around the exciting laser focus as depicted in Figure 4B. Particularly, by introducing a depletion beam the linewidth was more than halved from 155 to 65 nm, compared to the diffraction-limited printing of the same photoresist (Figure 4C).[13]

We recently reported a one-component photoresist, based on a copolymer of methyl methacrylate and spirothiopyran (STP)-functionalized methacrylate.[16] STP is a photoswitch and can be excited to undergo ring opening to its merocyanine (MC) derivative via two-photon absorption at 820 nm (Figure 4D). Subsequently, the MC moieties in the photoresist form physical crosslinks via supramolecular interactions, allowing for the fabrication of free-standing 3D structures. Furthermore, irradiation at 640 nm promotes the relaxation of MC back to STP. Hence, the lower wavelength was employed as a new parameter to increase the resolution and enabled a decrease of the printable linewidth from 55 to 31 nm.[16] In general, the light-induced switching of photoswitches between a reactive and an unreactive state offers great opportunities for antagonistic systems. Another very promising example was introduced by us last year and is based on the reaction of a diarylethene photoswitch with an *o*-MBA.[38]

In the past few years, the motivation to break past the diffraction-limit for 3D printing by relying on antagonistic photochemistry, resulted in many publications on the topic.[16,31,34,38] Pushing the achievable resolution to its limit is of exceptional interest as it would offer extremely precise control over the fabrication of structures in the nanometer range with value for diverse applications, e.g., optical data storage with enhanced data density or 3D photonic metamaterials.[35]

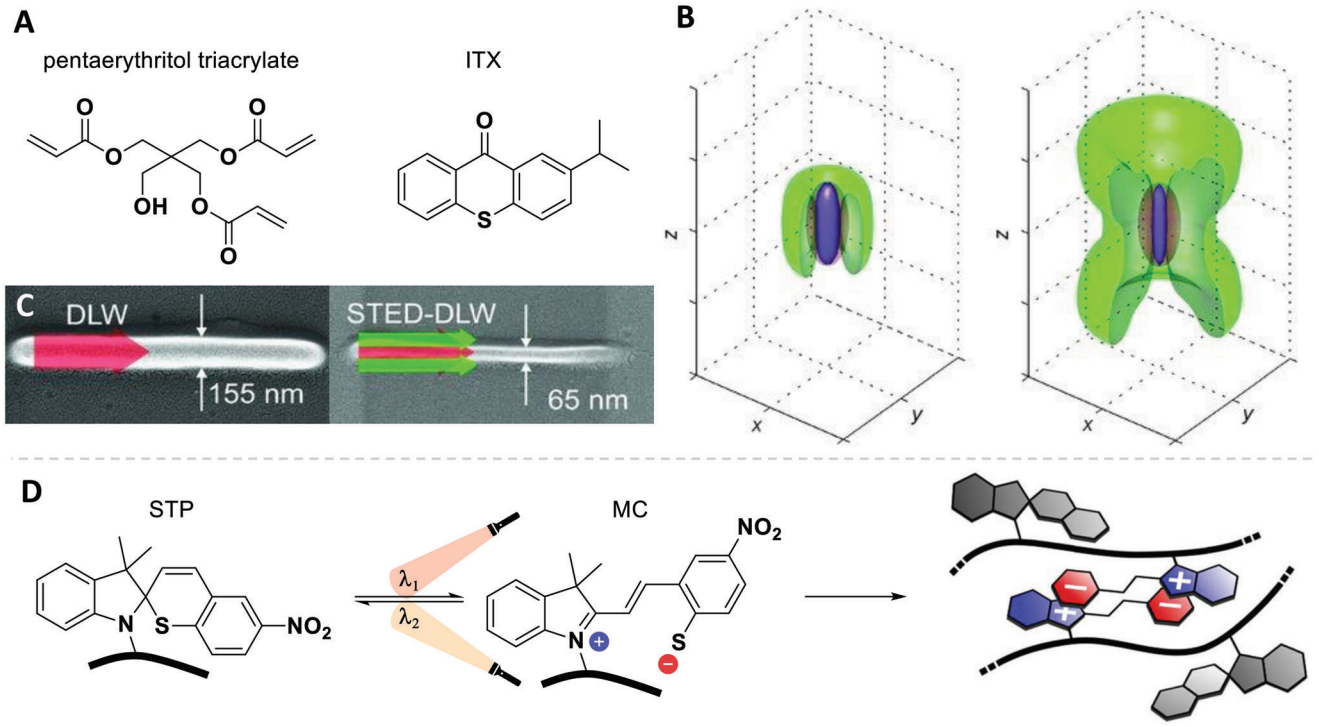

Figure 4. A) Components of the photoresist for STED-inspired 3D printing, i.e., monomer pentaerythritol triacrylate and photoinitiator isopropyl thioxanthone (ITX). B) Calculated iso-intensity surfaces of the foci of the depletion laser (532 nm, green) and the excitation laser (810 nm, red). The blue surfaces illustrate regions in space that are sufficiently excited but not sufficiently depleted, corresponding to the effectively exposed regions. With increasing STED-power (compare left and right), the effectively exposed region shrinks. C) Polymer line width by two-photon printing of the same photoresist without (top, red arrow) and with addition of a depletion laser (bottom, green arrow). B,C) Reproduced with permission.[13] Copyright 2010, Wiley-VCH. D) Two-photon activated ring-opening of spirothiopyran (STP) at 820 nm (λ_1) to its merocyanine (MC) derivative. The reverse reaction is triggered by irradiation at 640 nm (λ_2). The merocyanine form can create physical crosslinks via supramolecular interactions. D) Adapted with permission.[16] Copyright 2019, American Chemical Society.

3. Printing with Multiple Colors of Light

Upon exploring recent advances in two-color 3D printing, the critical and diverse benefits of introducing a second wavelength become apparent. Adding a new parameter that can be modified grants enhanced control over the printing process. Nevertheless, this assertion is a significant understatement, since a second color of light not only allows for optimization of current manufacturing techniques, but rather paves the way for entirely new and superior printing approaches. Examples are the previously discussed light-sheet[11] (synergistic) and multimaterial printing[15] (orthogonal), as well as the STED-inspired high-resolution fabrication method[13] (antagonistic). Therefore, two-color photochemistry constitutes a highly relevant topic with enormous potential for additive manufacturing. However, this raises the question of what would be achievable with three, four, or even more colors of light?

3.1. Multi-Color Printing

The spectrum of light offers a wide range of new opportunities that can simultaneously be applied to fulfill defined individual purposes. Thus, more parameters are available, so the design of sophisticated systems with advanced functions becomes possible. Currently, the restricted versatility of materials a single printer can manufacture with a single resist greatly limits the commercial implementations for 3D printing. For instance, the design of a multimaterial photoresist that can be used to print disparate components from a single cartridge by employing different colors of light would revolutionize current 3D printing manufacturing processes. Consequently, complex structures for direct application could be realized in one fabrication step instead of manufacturing specific parts one by one and subsequently assembling these—including biomedical applications, e.g., the printing of organs or body parts, such as a retina. Furthermore, a universal photoresist would be extremely convenient due to its simplicity, perhaps making it even viable for household applications. That being said, versatile 3D printing is also very attractive to the field of space travel, which struggles with mass and space constraints, as well as limited access to most resources due to remoteness. The possibility to apply a photoresist on a "one-size-fits-all" basis for diverse tailoring of the desired structures would bring great advantages under these limited conditions.

In addition to enhancing the control over either synergistic, orthogonal, or antagonistic interactions of light with a photoresist by introducing multiple wavelengths, the corresponding fusions are also thinkable. For example, multimaterial printing could be performed very fast (orthogonal + synergistic) or extremely precise (orthogonal + antagonistic). Moreover, even though a combination of synergistic and antagonistic photochemistry may seem

contradictory at first glance, if these processes are λ-orthogonal, large objects with extremely fine details could be fabricated in a short time. Clearly, these processes are currently science fiction. For them to become science fact, our understanding of photochemical behaviors of reactive chromophores needs to strongly increase, particularly in light of the evident disparity of their absorption spectra with their photochemical action plots, which we have demonstrated over the last decade.[8] We submit that the generation of action plots is mandatory for every photochemical reaction system, as the absorption spectra cannot be relied on for predicting chemical reactivity.

3.2. Introduction of Stimuli Responses

Apart from the innovative techniques with improved control during the printing process, the next step is to influence an object after it has been printed. This concept is known as 4D printing and describes the evolution of shape, property, and functionality of a 3D printed structure in the fourth dimension of time under a predetermined stimulus, e.g., temperature, pH value, or light intensity.[21,39] For example, the grabbing motion of a gripper arm can be recreated by the photoinduced bending of a printed structure which does not contain any electronic based materials.[40] Light has a key advantage over the other stimuli, due to its unprecedented spatiotemporal control which is critical in order to precisely trigger localized changes of the printed structure even on the micro- and nano-scale.[3–5] Furthermore, the spectrum of light gives the opportunity to work with a wide range of different wavelengths with the potential to trigger disparate effects. As the number of colors that can trigger diverse changes of a 4D printed object increases, so do the ways to control it. The result is a remote control with many buttons for precise regulation of various functions, e.g., specific movements of a robot. For the design of such materials, 3D laser printing is a very valuable tool since objects with a defined stimuli response can be fabricated in a tailored and straightforward manner.[41] For the printed structure, light offers the necessary spatiotemporal regulation for accurate activation of desired responses even in diminutive areas. One theoretical example is 4D printing of nanorobots that could perform increasingly complex tasks with each new stimulating wavelength, the equivalent of adding a new button on a remote control.[42] Consequently, the ease of producing customized structures via 3D printing, combined with the introduction of responsiveness to multiple wavelengths of light, offers great potential for multi-color 4D printing.[4]

3.3. Problems and Approaches to Solutions

Currently, two-color 3D printing is still in its infancy and does not yet play a role in commercial applications due to the intricate and complex nature of multi-color photochemistry. Introducing even more colors sharply increases the photochemical complexity due to several reasons. First, it is important to keep in mind that λ-orthogonal reactivities are not defined by the absorption spectra of chromophores, but by their action plots.[8] These reactivities, do not correspond to defined wavelengths only, but always to ranges that are prone to overlap, resulting in a loss of λ-orthogonality and consequently the control over the process.[4] The next issue is closely related, since most chromophores exhibit overlapping reactivities in the energy-rich UV range that cannot be triggered independently of each other.[43] Further, UV light also has the problem of low penetration depth and harmfulness to biological tissues.[43,44] Therefore, the visible light spectrum carries the greatest potential for multi-color techniques. Unfortunately, only few chromophores are activated in the visible range, which strongly narrows down the feasible options.[43]

These issues now raise the question of how we can harness the opportunities in multi-color photochemistry. For instance, it is of utmost importance to red-shift (without the need of catalysts) photochemical reactivity into the visible part of the spectrum by developing and discovering novel photoreactive compounds. Furthermore, red shifting already known chromophores by redesigning and tuning these is another very important approach.[43,45] Moreover, as noted above, it is critical to be aware that absorption does not coincide with reactivity.[8] In summary, to create complex multi-color systems, the library of available chromophores in the visible light region needs to be expanded, and to efficiently search for λ-orthogonal windows, it is essential to perform thorough action plot studies.[8,43]

4. Conclusion and Outlook

By its nature, light provides the ability of spatiotemporal control over chemical processes.[3–5] The use of multiple colors significantly expands subsequent control options and opens up extraordinary new opportunities, especially in the field of 3D printing.[4] Herein, the great versatility and potential of 3D printing with two colors of light were elucidated by introducing current breakthroughs and novel approaches in the field. Generally, the photochemistry behind these fabrication processes is based on one of three interactions between light and photoresist, i.e., synergistic, orthogonal, or antagonistic.[8]

Synergistic photochemistry requires simultaneous irradiation with two different wavelengths in order to trigger a reaction. This requirement has been exploited to develop intriguing new linear volumetric 3D printing approaches (i.e., light sheet-printing[11] and xolography[12]) with potential accuracy on the microscale, while being orders of magnitude faster and less expensive than two-photon techniques.[11] In the case of orthogonal light-matter interactions, separate crosslinking reactions are induced by different wavelengths and proceed completely independently of each other.[15,29] Consequently, the fabrication of multimaterial objects from a single ink cartridge is enabled.[15] Antagonistic 3D printing relies on the contrary effects of different colors of light on a photoresist. These competing interactions with light allow for high resolution printing (inspired by STED)[13,16,35,37] of complex structures on the micro- and nano-scale below the diffraction limit.[16,31]

Furthermore, the impact and opportunities of moving from two colors to multiple colors of light were discussed. More wavelengths mean access to more parameters that can be influenced, which increases the control and versatility of a printing process, e.g., orthogonal printing of complex multimaterial structures from one photoresist with different colors of light. Additionally, combinations of synergistic, orthogonal, and antagonistic techniques to merge the corresponding benefits are conceivable.

Apart from 3D printing, multi-color systems are also very promising for the manipulation of light-responsive 4D structures. Control over multiple wavelengths offers the opportunity for intricate manipulation, even on the micro- and nano-scale, e, for realizing nanorobots.

However, two-color 3D printing is still in its infancy and the introduction of additional colors is an extremely challenging task. To take on this challenge, it is vital to step out of the UV range where reactivities of most photoactive compounds overlap and λ-orthogonality is highly challenging. Therefore, in-depth research on red shifting and designing new chromophores in the visible light range is necessary. In addition, extensive action plot studies need to be performed in order to identify reactivities and λ-orthogonal windows of the chromophores.

Particularly photoswitches will become key players for the development of multi-color systems due to their inherent nature to reversibly change the chemical structure under irradiation at distinct wavelengths. In order to ensure continuous control over a system, this reversibility is critical and cannot be realized by solely relying on "one-way" photoreactions, e.g., photodeprotection. All in all, the subject of multi-color printing is extremely broad and will require the collaborative efforts of experts ranging from the fields of organic and polymer chemistry, laser physics to materials science. To finally answer the question from the introduction: The future will be bright.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

C.B.-K. acknowledges funding from the Australian Research Council (ARC) in the form of a Laureate Fellowship (FL170100014) enabling his photochemical research program as well as continued key support from the Queensland University of Technology (QUT). E.B., C.B.-K., and M.W. acknowledge additional funding by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy for the Excellence Cluster "3D Matter Made to Order" (EXC-2082/1–390761711), by the Carl Zeiss Foundation, and by the Helmholtz program "Materials Systems Engineering".

Open access publishing facilitated by Queensland University of Technology, as part of the Wiley - Queensland University of Technology agreement via the Council of Australian University Librarians.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

3D laser lithography, 3D printing, photochemistry

Received: August 30, 2022
Revised: October 3, 2022
Published online:

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