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Cooperative Network Formation via Two-Colour Light-Activated λ-Orthogonal Chromophores

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Abstract: Independently addressing photoreactive sites within one molecule with two colours of light is a formidable challenge. Here, we combine two sequence independent λ-orthogonal chromophores in one hetero-telechelic dilinker molecule, to exploit their disparate reactivity utilizing the same reaction partner, a maleimide-containing polymer. We demonstrate that polymer network formation only proceeds if two colours of light are employed. Upon single colour irradiation, linker-decorated post-functionalized polymers are generated at either wavelength and in either sequence. Network formation, however, is only achieved by sequential or simultaneous two colour irradiation. The herein introduced photoreactive system demonstrates the power of wavelength orthogonal chemistry in macromolecular synthesis.

Introduction

One of the most critical challenges in synthetic chemistry is to control chemical reactions such that the molecular design controls the material's function.[1] A diverse set of external stimuli such as temperature, pH, catalyst and light can be employed to control a chemical reaction if an appropriate functional group is present.[2] Light stimulation sets itself apart from other external stimuli through its unique spatio-temporal control and non-invasive nature.[3] Critically, light has the potential to propel a specific reaction by adjustment of wavelength and intensity without affecting other present light-active compounds.[4] Such reactions have been termed λ-orthogonal.[5]

A sequence-independent λ-orthogonal system (also termed fully λ-orthogonal system) comprising two chromophores requires the activation of only one chromophore during the exposure with a specific colour of light, while the other one remains inactive, irrespective of the irradiation sequence in which the two colours of light are employed.[6] Currently, sequence-dependent λ-orthogonal systems are predominant since most visible light responsive chromophores also react at shorter wavelengths (i.e. higher energies). Thus, there is an ongoing interest in the design of visible light active chromophores, which exhibit low or no reactivity under UV light. As a response to meet this demand, our group has recently reported a blue-green light activated tetrazole, *N,N*-(dimethyl)-aminopyrene aryl tetrazole (APAT). By using dimethylamino-functionalized pyrene as tetrazole-substituent instead of an N-aryl moiety,[7] extension of the conjugated system of tetrazole with pyrene and introduction of an electron donating dimethylamino group was achieved, both of which are conventionally used strategies to bathochromically shift the absorptivity and reactivity. APAT undergoes a nitrile imine-mediated tetrazole-ene cycloaddition (NITEC) reaction, which can be conducted with a maleimide reaction partner fully orthogonally in the presence of the photoenolization/Diels–Alder (PEDA) reactant *o*-methylbenzaldehyde (*o*MBA) as a competitive reactant for the maleimide.[8]

λ-Orthogonal ligation reactions in a one-pot system have also sparked interest in macromolecular sciences due to their simplicity. Potentially complex procedures can be avoided by eliminating the need for catalysts and additives.[9] With regard to light-gated network formation, two colours of light have been utilized to generate interpenetrating networks (IPNs), where one network is formed with one color of light and the second network is formed with the second colour. This principle has been demonstrated for chain growth networks initiated with pathway-dependent orthogonal photoinitiators on the one hand[11] and with uncatalyzed pathway-dependent orthogonal photoligation reactions on the other hand.[12] While the full IPN only forms in the presence of two colours of light, network formation in general already occurs upon irradiation with one colour. To achieve strictly dual colour network formation, interconnected conditional reactive reaction paths are necessary as

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they have been utilized in light-sheet printing[13] and xolography.[14]

Furthermore, λ-orthogonal ligation of macromolecular precursors with heterotelechelic linkers provides ready access to complex macromolecular architectures.[10] For example, a bichromophoric molecule containing *o*MBA at one end and a vinylpyrene derivative at the other end was used to λ-orthogonally address both chromophores. Dimerization of vinylpyrenes through cycloaddition and thereby ligation of two heterotelechelic linkers with each other was achieved in the visible light region. Due to the photo-reversible character of this reaction upon UV irradiation, the eventually formed dimer dissociates again, while an irreversible cycloadduct formation occurs between *o*MBA and maleimide.[10a] Our team also introduced a heterotele-chelic linker bearing one *o*MBA and one tetrazole photo-reactive terminus, which both undergo reactions with maleimides. While both of these ligations are irreversible and therefore allow ligation of the three units, the set of λ-orthogonal reactions can only be conducted consecutively, activating the *o*MBA prior to the tetrazole. The dilinker has been utilized for block-copolymer synthesis through sequence-dependent λ-orthogonal reactions in the presence of maleimide end-functionalized polymers.[10b] The same tele-chelic linker was later used to synthesize star polymers in the presence of a trifunctional maleimide.[10c] While these examples already show an impressive degree of control, the orthogonal chromophores so far rely on sequence-dependent reactions. Employing sequence-independent λ-orthogonal chromophore pairs like APAT/*o*MBA in such systems, however, will enable perfect photochemical control and therefore the design of advanced soft matter materials.

Herein, we combine a sequence-independent λ-orthogonal chromophore-pair in a heterotelechelic dilinker to exploit their cooperative photoreactivity allowing the formation of a crosslinked network exclusively when exposed to two colours of light. This cooperative photoreaction mechanism differs significantly from synergystic reactions, where two photoactivation steps are required to form one covalent bond, requiring the simultaneous presence of two colours of light.[5a,15] In cooperative reactions, each of the two photoactivation steps can cause bond formation independently. As a result, both sequential and simultaneous two colour irradiation, are possible ways to react both chromophores. As a pivotal component of the new cooperative photochemical system, a heterotelechelic dilinker based on poly(ethylene glycol) (PEG) was synthesized bearing two fully λ-orthogonal chromophores, i.e. APAT at one end and *o*MBA at the other end. A polymer decorated with maleimide units (**P**) is used as a reaction partner. The APAT terminus of the heterotelechelic dilinker can undergo a NITEC reaction with maleimides in the visible light regime (450 nm), while *o*MBA does not absorb and react. Conversely, UV light (325 nm) activates *o*MBA to perform a PEDA reaction with maleimides, while APAT remains inactive. Single colour irradiation therefore only leads to polymer-modification through functionalization with the respective chromophore. Irradiation with two colours either in a sequence-independent step wise, or in a simultaneous fashion activates both terminal chromophores of the heterotelechelic dilinker and causes both chromophores to react with **P** in a cooperative fashion, resulting in the formation of a crosslinked network (Scheme 1). Therefore, the heterotelechelic dilinker only functions as a crosslinker in the presence of two colours of light for the desired cooperative network formation. To the best of our knowledge, the described photochemical reaction system is the first to employ a fully λ-orthogonal chromophore pair for cooperative network formation under the influence of two colours of light.[16]
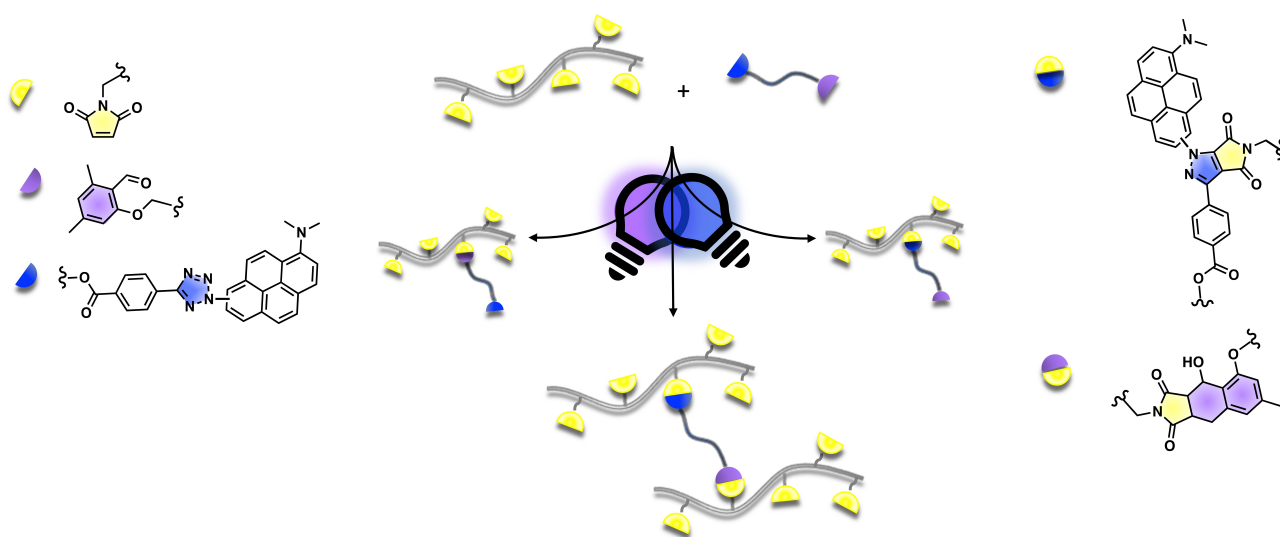
Scheme 1. Representation of the photochemical polymer postmodification in the presence of one colour of light and cooperative network formation in the presence of two colours of light through irradiating the mixture of a maleimide-containing polymer and a heterotelechelic dilinker featuring two fully sequence-independent λ-orthogonal chromophores with UV (325 nm) and/or blue (450 nm) LEDs.

Results and Discussion

Synthesis of Cooperative Photochemical System Components

The fully orthogonal chromophores were linked using a linear monodisperse PEG to employ these λ-orthogonal chromophores in a cooperative photochemical system. The heterotelechelic dilinker (*o*MBA-PEG-APAT) was synthesized in two steps from monodisperse azido-PEG19-alcohol. The long PEG-spacer was chosen to enhance the overall solubility of the final heterotelechelic macromolecular dilinker since APAT itself exhibits rather poor solubility in most solvents. Moreover, the utilization of azido-PEG19-alcohol enabled the facile azide-alkyne driven attachment of APAT, which is otherwise difficult to react to full conversion due to solubility problems. Subsequently, the carboxylic acid-substituted *o*MBA was attached to the hydroxyl end of PEG via Steglich esterification (for detailed synthetic procedures refer to the Supporting Information Section 1.3).

The maleimide-containing polymer **P**, which is utilized as a ligation partner for all photoligation experiments, was synthesized via copolymerization of methyl methacrylate and furan-protected maleimide acrylate monomers by ATRP (for detailed synthetic procedures refer to the Supporting Information Section 1.3). ATRP polymerization was employed to achieve a narrow polydisperse polymer, which facilitates monitoring of the photoligation reactions between **P** and *o*MBA-PEG-APAT with one colour irradiation, as well as the network formation with two colour irradiation via SEC. The choice of molecular weight of the polymer was underpinned by the aim to achieve a sufficient number of maleimide units per polymer chain to induce crosslinking even at moderate conversions.

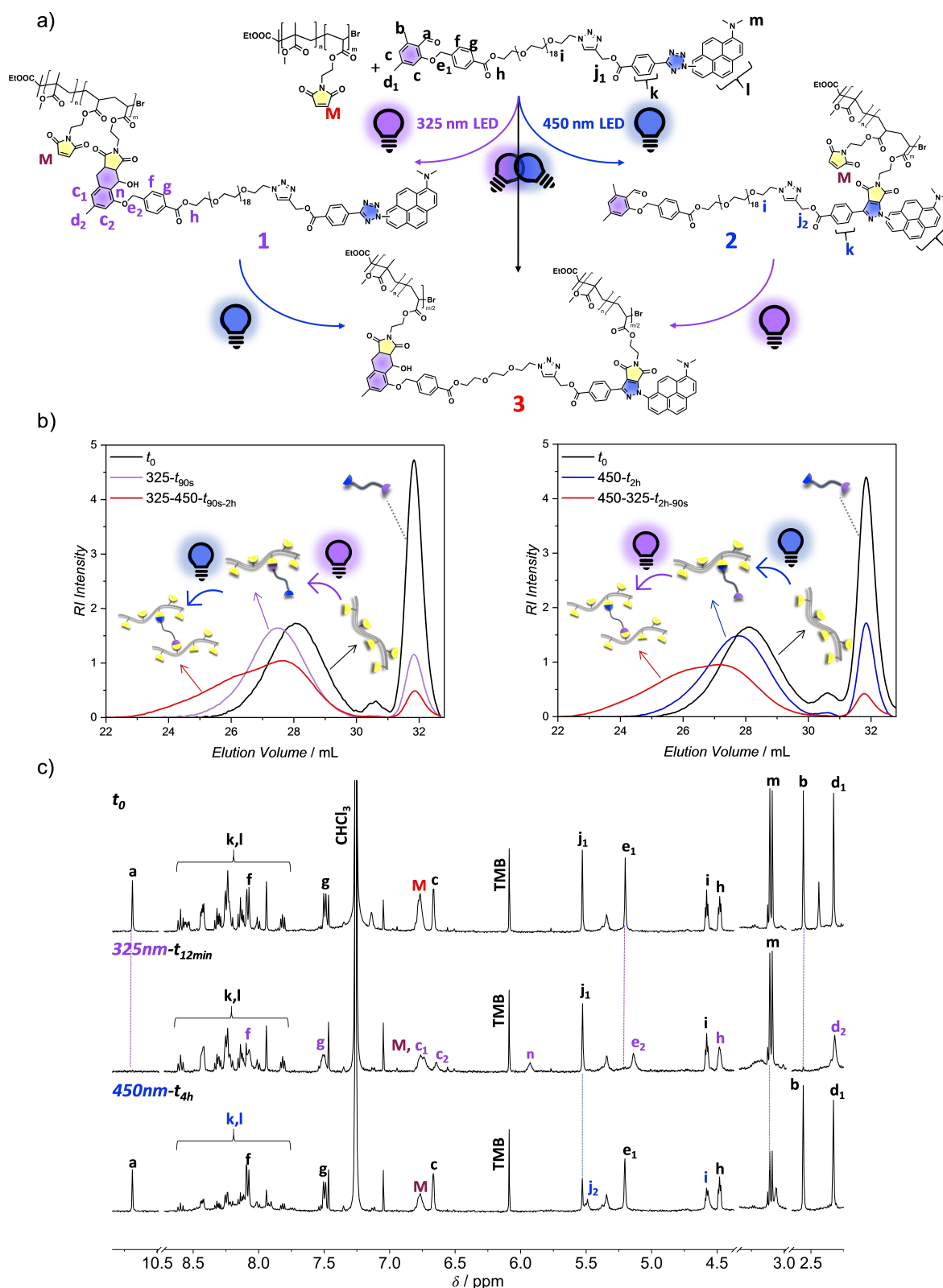### Sequential Two-Colour Irradiation

To investigate if the polymer network is generated cooperatively, initially, sequential two colour irradiation experiments were performed for **P**/*o*MBA-PEG-APAT mixtures. Under conditions of full λ-orthogonality, crosslinking only occurs after the reaction mixture has been exposed to both colours of light (Figure 1a). Thus, the reaction mixtures were analyzed after each irradiation step via SEC (Figure 1b) and ^{1}H NMR spectroscopy (Figure 1c, refer to Supporting Information Section 2.1.1). Initial single colour irradiation induced a cycloaddition between the respective end chromophore of *o*MBA-PEG-APAT and **P**, resulting in post-functionalized polymers. The conservation of the molecular weight dispersity of the polymer before and after irradiation with a single colour of light demonstrates that no crosslinking takes place. It is critical to generate substantial conversion to the post-functionalized polymers **1** and **2**, to ensure that the respective side of the heterotelechelic dilinker is close to quantitatively attaching to **P** after single colour irradiation. Only then *o*MBA-PEG-APAT will crosslink **P** upon irradiation with the second colour of light. The conversion to the cycloadduct (**1** and **2**) was approximated by the reduction of the area of the heterotelechelic dilinker peak in the SEC elugram. To follow the change in this peak accurately, identical volumes of reaction mixtures were injected for all samples before and after irradiation, eliminating the neccesity for standards. The conversion was calculated as 75% for the formation of **1** after 325 nm LED irradiation for 90 s and 65% for the generation of **2** after 450 nm LED irradiation for 2 h, which were found to be sufficient to continue with the subsequent irradiation using the second colour of light to observe the network formation. Subsequent irradiation with the second colour of light shows an increase in molecular weight dispersity of **P** and a high molecular weight shoulder in SEC elugrams, which can be attributed to the onset of network formation (Figure 1b and Table S1). The results prove that the sequential two colour irradiation produces a crosslinked network (**3**) through the cooperative reactivity of both chromophores of the heterotelechelic dilinker.

The above described experiments were monitored by ^{1}H NMR spectroscopy to further confirm that no crosslinking occurs after exposure to only one colour, which can be substantiated if the chromophores of *o*MBA-PEG-APAT react with **P** in a sequence independent λ-orthogonal way (Figure 1c, also refer to Supporting Information Section 2.1.1). Indeed, ^{1}H NMR spectroscopic analyses demonstrate that the irradiation of a **P**/*o*MBA-PEG-APAT mixture with the 325 nm LED for 12 min only activates *o*MBA to form compound **1** through the PEDA reaction, which can readily be established via the disappearance of the aldehyde (a) and one the of the methyl groups (b) of *o*MBA. Additionally, a new resonance formed at 5.93 ppm (n) and splitting of the aromatic resonances of *o*MBA (c into c_1 and c_2) as well as broadening of the resonances associated with aromatic protons of the benzene ring attached to *o*MBA (f, g) was evident. The methylene protons next to the isoindole unit formed after cycloaddition between *o*MBA and maleimide appears as a new broad signal (e_2) replacing the signal (e_1). However, the integrals of indicative signals of APAT (j_1, k, l, m) remained unchanged after 325 nm irradiation.

Irradiation of a **P**/*o*MBA-PEG-APAT mixture with the 450 nm LED activated APAT, but not *o*MBA, resulted in the generation of compound **2** through a NITEC reaction (Figure 1c, also refer to Supporting Information Section 2.1.1). Changes in the ^{1}H NMR spectrum after pyrazole cycloadduct formation were evident through the broadening of the APAT aromatic resonances (k,l), a decline of the original methyl proton integral of APAT (m), and a new broad signal (j_2) formation for the methylene protons beside the pyrazole cycloadduct replacing the signal (j_1). However, the integrals associated with the characteristic resonances of *o*MBA (a, c, b, d_1, e_1, f, g, h) remained unaltered. Thus, the photoactivation of each chromophore occurs independently and crosslink formation upon single colour irradiation was categorically excluded.

After single colour irradiation either with a 325 nm or with a 450 nm LED, maleimide overconsumption was noticed in the NMR spectra, i.e. more maleimide was consumed than either *o*MBA or APAT needs to react at full conversion. To elucidate the cause, irradiations of solely **P** on the one hand and of a solution of the small molecule

Figure 1. a) Formation of post-functionalized polymers with only single colour irradiation (**1**, **2**) and cooperative network formation upon either sequential or simultaneous two colour irradiation (**3**), b) SEC elugrams for the initial single colour and sequential two colour irradiation of **P/oMBA-PEG-APAT**. The reaction mixtures were initially irradiated with the 325 nm LED and subsequently with the 450 nm LED, or vice versa, c) ^{1}H NMR spectra (CDCl$_3$, 500 MHz) before and after irradiation of the **P/oMBA-PEG-APAT** mixture with a single colour of light using a 325 nm LED or a 450 nm LED, respectively. TMB denotes trimethoxybenzene, which was utilized as internal standard.

maleimide on the other hand with either colour were performed (refer to Supporting Information Section 2.1.2). These experiments suggest that the overconsumption is a result of intramolecular maleimide dimerization within **P**. Since dimerization was only observed at 325 nm in the control experiments, we hypothesize that an excited state energy transfer in the presence of APAT results in side reactions causing internal maleimide overconsumption also at 450 nm in the heterotelechelic dilinker irradiation experiments. SEC results of the control experiments show a shift towards lower molecular weights upon 325 nm irradiation, which suggests that dimerization occurs only intramolecularly within **P**. Therefore, this side reaction neither prematurely crosslinks **P** upon irradiation with one colour nor does it hinder the intended network formation with two colours. With a simple adjustment of the stoichiometry of **P** and the heterotelechelic dilinker, it is ensured that sufficient maleimide units are available for successful crosslinking (refer to Supporting Information Section 2.1.2, Table S3).

Simultaneous Two-Colour Irradiation

Upon evidencing that the polymer network is only generated cooperatively with two colours of light and not with one colour, photochemical cooperative network formation was explored with simultaneous two colour irradiation. Here, it is critical to ensure that both the PEDA and the NITEC reaction occur within a similar time-frame. Otherwise, the PEDA reaction will be completed much earlier than the NITEC reaction due its higher reaction quantum yield and the limitation of 450 nm light intensity inherent to the LED light source. Therefore, the PEDA reaction rate was decreased by reducing the 325 nm LED flux. To approximate by which factor the rate of the PEDA reaction needed to be reduced, **P/oMBA-PEG-APAT** mixtures were subjected to single colour irradiation either with a 325 nm or a 450 nm LED for various times (refer to Supporting Information Section 2.1.3). Subsequently, concentration vs time graphs were established displaying the consumption of the chromophores during the course of both reactions (Figure S34). Through the analyses of the reaction kinetics data, it was established that the rate of the PEDA reaction requires a deceleration of a factor of approximately 13 to be able to reach a half-life equivalent to that of the NITEC reaction within a similar time-frame (refer to Supporting Information Section 2.1.3). Therefore, the flux of the 325 nm LED was reduced by a factor of 13 for the following simultaneous two colour irradiation experiments.

After simultaneous two-colour irradiation for 6 h, the molecular weight dispersity of **P** increased and the formation of a higher molecular weight shoulder was observed, demonstrating that the cooperative photochemical system commences to crosslink by linking of polymer chains **P** with each other via **oMBA-PEG-APAT** (Figure 2, Table S4). It is critical to demonstrate that the network only forms cooperatively with dual colour irradiation. Therefore, single colour irradiation experiments were also performed using the same conditions. As intended, the SEC elugrams exhibit a shift towards high
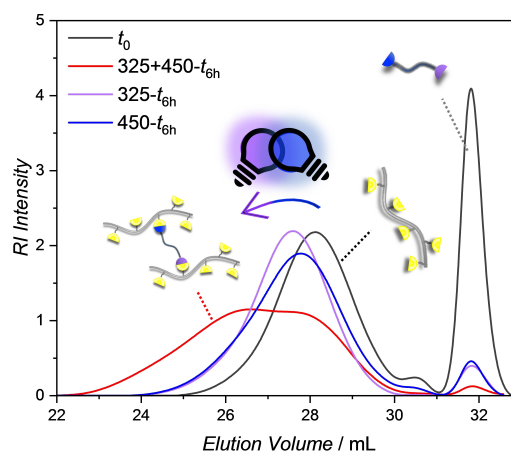
Figure 2. SEC monitoring for single colour and simultaneous two-colour irradiation of **P/oMBA-PEG-APAT** at 325 and/or 450 nm.

molecular weight due to attachment of the heterotelechelic dilinker to **P** on one side. However, there is no significant change in molecular weight dispersity (Figure 2, Table S4). Thus, it is once more demonstrated that the network only forms cooperatively via two colour irradiation and not with single colour irradiation. To further evidence that both of the chromophores are simultaneously activated, and cooperative crosslinking occurs from the very start of irradiation on, kinetic experiments were conducted for the **P/oMBA-PEG-APAT** mixture by irradiating it with two colours of light for various durations up to 6 h. The aforementioned SEC results indicative of crosslinking were observed for all time points, showing that the crosslinking occurs through simultaneously triggered photoreactions (Figure S35, also refer to Supporting Information Section 2.1.4).

To obtain visual proof for the crosslinking behaviour, the simultaneous two-colour irradiation experiments were performed with the 15-fold concentration of both, **P** and **oMBA-PEG-APAT**. To establish if full orthogonality of the two photoinduced reactions can be maintained at such high concentrations, analogous single colour irradiation experiments were carried out. Crosslinking was identified unambiguously in the presence of two colours. For the single colour irradiation at 450 nm, minimal network formation is also observed (Figure S36, Figure S37), suggesting that the APAT excited state species may sensitize *o*MBA and thus trigger PEDA reactions at high concentrations. While this somewhat compromises wavelength orthogonality, the judicious combination of concentration and irradiation conditions allows to maintain orthogonality to a high degree, as potential sensitization exhibits a quadratic dependence on the distance between two molecules. Further optimization of the system for high concentration regimes requires the consideration of several key parameters (e.g. concentration range, adjustment of the intensity of the 450 nm LED, sample thickness). Such a complex optimization lies beyond the scope of our current proof of concept study, falling well into the realm of photoresists design.

Conclusion

In summary, a heterotelechelic dilinker comprising the fully λ-orthogonal chromophores *o*MBA and APAT was synthesized. Using a maleimide-containing polymer, the heterotelechelic dilinker was exploited in a sequence-independent λ-orthogonal fashion upon irradiation with one colour of light. In the presence of two colours of light, cooperative network formation was achieved. Critically, we demonstrate that both sequential and simultaneous dual colour irradiation induce the formation of a crosslinked network in a cooperative fashion. Initial studies at high concentrations suggest that the cooperativity can be maintained to a high degree under such conditions. Thus, the results obtained herein provide critical insights to design criteria for photoresists in 3D light sheet printing that requires dual colour activation.[13b,14,17]

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

[1] a) A. Shahrokhinia, P. Biswas, J. F. Reuther, *J. Polym. Sci.* **2021**, *59*, 1748–1786; b) H. Frisch, D. E. Marschner, A. S. Goldmann, C. Barner-Kowollik, *Angew. Chem. Int. Ed.* **2018**, *57*, 2036–2045.

[2] a) N. Corrigan, C. Boyer, *ACS Macro Lett.* **2019**, *8*, 812–818; b) N. Corrigan, J. Yeow, P. Judzewitsch, J. Xu, C. Boyer, *Angew. Chem. Int. Ed.* **2019**, *58*, 5170–5189.

[3] a) B. D. Fairbanks, L. J. Macdougall, S. Mavila, J. Sinha, B. E. Kirkpatrick, K. S. Anseth, C. N. Bowman, *Chem. Rev.* **2021**, *121*, 6915–6990; b) F. A. Leibfarth, K. M. Mattson, B. P. Fors, H. A. Collins, C. J. Hawker, *Angew. Chem. Int. Ed.* **2013**, *52*, 199–210; c) S. Aubert, M. Bezagu, A. C. Spivey, S. Arseniyadis, *Nat. Chem. Rev.* **2019**, *3*, 706–722; d) J. Schwartz, A. Boydston, *Nat. Commun.* **2019**, *10*, 791; e) C. Brieke, F. Rohrbach, A. Gottschalk, G. Mayer, A. Heckel, *Angew. Chem. Int. Ed.* **2012**, *51*, 8446–8476.

[4] a) N. Corrigan, M. Ciftci, K. Jung, C. Boyer, *Angew. Chem. Int. Ed.* **2021**, *60*, 1748–1781; b) S. Chatani, C. J. Kloxin, C. N. Bowman, *Polym. Chem.* **2014**, *5*, 2187–2201.

[5] a) I. M. Irshadeen, S. L. Walden, M. Wegener, V. X. Truong, H. Frisch, J. P. Blinco, C. Barner-Kowollik, *J. Am. Chem. Soc.* **2021**, *143*, 21113–21126; b) V. X. Truong, K. Ehrmann, M. Seifermann, P. A. Levkin, C. Barner-Kowollik, *Chem. Eur. J.* **2022**, *28*, e202104466.

[6] a) C. G. Bochet, *Isr. J. Chem.* **2021**, *61*, 486–495; b) P. Lu, D. Ahn, R. Yunis, L. Delafresnaye, N. Corrigan, C. Boyer, C. Barner-Kowollik, Z. A. Page, *Matter* **2021**, *4*, 2172–2229.

[7] P. W. Kamm, L. L. Rodrigues, S. L. Walden, J. P. Blinco, A.-N. Unterreiner, C. Barner-Kowollik, *Chem. Sci.* **2022**, *13*, 531–535.

[8] P. W. Kamm, J. P. Blinco, A.-N. Unterreiner, C. Barner-Kowollik, *Chem. Commun.* **2021**, *57*, 3991–3994.

[9] G. S. Kumar, Q. Lin, *Chem. Rev.* **2021**, *121*, 6991–7031.

[10] a) D. E. Marschner, C. O. Franck, D. Abt, H. Mutlu, C. Barner-Kowollik, *Chem. Commun.* **2019**, *55*, 9877–9880; b) K. Hiltebrandt, T. Pauloehrl, J. P. Blinco, K. Linkert, H. G. Börner, C. Barner-Kowollik, *Angew. Chem. Int. Ed.* **2015**, *54*, 2838–2843; c) K. Hiltebrandt, M. Kaupp, E. Molle, J. P. Menzel, J. P. Blinco, C. Barner-Kowollik, *Chem. Commun.* **2016**, *52*, 9426–9429.

[11] a) N. D. Dolinski, E. B. Callaway, C. S. Sample, L. F. Gockowski, R. Chavez, Z. A. Page, F. Eisenreich, S. Hecht, M. T. Valentine, F. W. Zok, *ACS Appl. Mater. Interfaces* **2021**, *13*, 22065–22072; b) X. Fernández-Francos, O. Konuray, X. Ramis, À. Serra, S. De la Flor, *Materials* **2020**, *14*, 107; c) X. Zhang, W. Xi, S. Huang, K. Long, C. N. Bowman, *Macromolecules* **2017**, *50*, 5652–5660; d) I. Cazin, M. O. Gleirscher, M. Fleisch, M. Berer, M. Sangermano, S. Schlögl, *Addit. Manuf.* **2022**, *57*, 102977.

[12] a) V. X. Truong, M. P. Ablett, S. M. Richardson, J. A. Hoyland, A. P. Dove, *J. Am. Chem. Soc.* **2015**, *137*, 1618–1622; b) L. Michalek, S. Bialas, S. L. Walden, F. R. Bloesser, H. Frisch, C. Barner-Kowollik, *Adv. Funct. Mater.* **2020**, *30*, 2005328.

[13] a) V. Hahn, P. Rietz, F. Hermann, P. Müller, C. Barner-Kowollik, T. Schlöder, W. Wenzel, E. Blasco, M. Wegener, *Nat. Photonics* **2022**, *16*, 784–791; b) V. Hahn, F. Mayer, M. Thiel, M. Wegener, *Optics Photonics News* **2019**, *30*, 28–35.

[14] M. Regehly, Y. Garmshausen, M. Reuter, N. F. König, E. Israel, D. P. Kelly, C.-Y. Chou, K. Koch, B. Asfari, S. Hecht, *Nature* **2020**, *588*, 620–624.

[15] S. L. Walden, L. L. Rodrigues, J. Alves, J. P. Blinco, V. X. Truong, C. Barner-Kowollik, *Nat. Commun.* **2022**, *13*, 2943.

[16] P. Xiao, J. Zhang, *3D Printing with Light*, Walter de Gruyter, GmbH & Co KG, **2021**.

[17] a) C. Darkes-Burkey, R. F. Shepherd, Nature Publishing Group UK London, *High-resolution 3D Printing in Seconds* **2020**; b) J. Hobich, E. Blasco, M. Wegener, H. Mutlu, C. Barner-Kowollik, *Macromol. Chem. Phys.* **2023**, *224*, 2200318.