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Light-Stabilised Dynamic Materials

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ABSTRACT: The light-responsive adaptation of polymer materials typically requires different wavelengths or additional heat to induce reversible covalent bond formation and dissociation. Here, we bypass the use of invasive triggers by introducing *light-stabilised dynamic materials* that can undergo a repeatable change in topology from a covalently crosslinked material into a liquid polymer formulation by switching one visible light source on-and-off without the need for any additional triggers. Specifically, we exploit the photo-Diels-Alder reaction of triazolinediones with naphthalenes as a dynamic covalent crosslinking platform that enables green light-induced network formation, while the crosslinked material collapses through spontaneous cycloreversion upon standing in the dark at room temperature. Importantly, the covalent crosslinks remain stabilised for as long as visible light is present, thereby retaining the material's structural integrity. This enables their potential use in an array of light-directed applications whereby network properties such as stiffness can be tuned by the mildest trigger of all: darkness.

INTRODUCTION.

The design of molecular systems that are capable to adapt and reorganise in response to external stimuli continues to highly impact fundamental chemistry research disciplines, most notably in the field of soft matter material sciences. In particular, photochromic systems play a pivotal role in providing switchable yet tailored mechanical, electronical and optical properties that can be externally controlled or even fuelled by light.[1-4] A truly fascinating application of photoswitchable dynamic behaviour can be found in molecular machines, where translational and rotary motion on the nanoscale can be achieved by continuously driving a photochemical system out-of-equilibrium by light.[5-10] Photoswitches – mainly based on azobenzene,[11-12] spiro(thio)pyran[13-14] or diarylethene motifs[15-16] – have further been successfully incorporated into bulk polymer materials,[17] for example to enable light-induced reversible colouration,[18-19] repeatable volume contraction/expansion[19-21] and even liquid-to-gel transitions.[22-23]

Although existing photoswitches can thus be employed to induce coherent property changes in polymer materials, these dynamic motifs are exclusively based on photoinduced isomerisation or intramolecular cyclisation reactions. Thus, no covalent bond formation and/or dissociation between two photoswitches can be directly accessed by light. From a material's perspective, achieving bond shuffling in polymer networks, for instance to enable healing that can be switched on/off by light, therefore implies molecular photoswitches to be combined with dynamic supramolecular interactions (e.g. azobenzene-cyclodextrin)[24] or even additional thermoreversible covalent systems (e.g. furan-maleimide).[25]

Alternatively, light-gated dynamic covalent bond formation and dissociation remains almost exclusively embedded into polymer materials through photoreversible cycloaddition reactions, archetypical [2+2] and [4+4] dimerisations of mainly cinnamates and anthracenes.[26-29] Whereas recent efforts have successfully been devoted to provide a toolbox of photocycloaddition reactions that can be triggered by lower energy visible light, inducing cycloreversion inherently requires elevated temperatures or high energy UV-irradiation and therefore often leads to thermal and photodamage of the materials or its surroundings.[30] Thus, the development of non-invasive stimuli that enable to tune both covalent bond formation as well as dissociation remains a grand challenge in the design of photodynamic systems. Indeed, adaptation by non-invasive triggers is particularly attractive for biological applications, where soft matter cell scaffolds have to be removed under ambient conditions once they become redundant,[31-32] or for subtractive 3D laser lithography photoresists, where support objects can be removed without chemical additives or an additional development step.[33-36]

Herein – rather than relying on two different wavelengths or an additional heating step – we pioneer an advanced light-switchable material that can be reversibly transformed from a covalently bound network into a liquid state, simply by switching one colour of light on-and-off, thus without the need for any additives or change in temperature. Our conceptual approach relies on a visible light-driven yet dynamic heteromolecular cycloaddition reaction, whereby the outcome remains near-quantitatively shifted to the covalently bound photoproducts, thereby generating a crosslinked material upon irradiation ($\lambda > 400$ nm, refer to Figure 1). Importantly, the thus formed cycloadducts are thermally labile and spontaneously dissociate upon standing in the dark at room temperature, yet remain intact under continued irradiation so that the material's crosslinking density can be retained for as long as the light is kept switched on.

Recently, Lehn and co-workers introduced the term photodynamic covalent bonds to describe small molecule covalent interactions that are stable under ambient temperature conditions, yet readily dissociate upon photoexcitation.[37] Here, we not only introduce the exact opposite strategy, but also validate our conceptual approach by the design of so-called *light-stabilised dynamic materials (LSDMs)*, wherein cleavage of a covalently crosslinked material into a viscous liquid is enabled by exploiting the mildest trigger of all, i.e. switching the lights off.

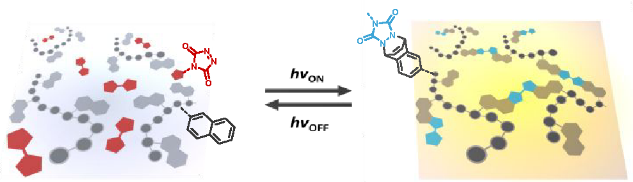


Figure 1. Devised light-stabilised dynamic materials, wherein a covalently crosslinked polymer material can be obtained through a visible light-driven cycloaddition (left to right), whereas the resulting network remains intact or light-stabilised under continuous irradiation (right). Simply switching the light off triggers the crosslinks to dissociate at room temperature through a spontaneous cycloreversion, thereby causing the material to collapse (right to left).

RESULTS AND DISCUSSION.

Model investigations. Our continued interest in the photochemical reactivity of triazolinediones (TADs) – powerful coupling reagents in (bio)organic and polymer chemistry[38] – led us to identify their visible light-induced cycloaddition to plain naphthalenes as a highly promising platform to devise light-stabilised dynamic materials (LSDMs). Indeed, while TAD and naphthalene do not readily react upon mixing, Kjell and Sheridan reported the formation of a thermally labile 1:1 addition product upon visible light irradiation, which they identified as the [4+2] cycloadduct (cf. Figure 2a).[39-40] In our hands, subjecting a solution of 4-*n*-butyl-TAD (**1**, 15 mM in CCl_4, Figure 2a) and plain naphthalene **2a** to green LED light ($\lambda = 515 – 525$ nm, 16 mW cm^{-2}) readily resulted in a colourless solution, whereby complete consumption of **1** into **3a** was evidenced from UV/vis and ^{1}H-NMR spectra recorded before and after irradiation (see Figures S1-S2). Moreover, the characteristic purple TAD colour rapidly reappeared upon switching the lights off and the initial starting reagents were regenerated.

While the TAD-naphthalene cycloaddition has recently gated the synthesis of theoretically interesting low molecular weight compounds,[41-42] a particular concern is the ability of TADs to undergo photopolymerisation when subjected to visible light.[43] In fact, we previously exploited this reversible self-polymerisation as a method to externally regulate the unique reactivity of TADs towards alkenes by transforming them into their deactivated polymeric state.[44] We thus first had to investigate whether the TAD-based cycloaddition with naphthalene suffered from competitive visible light-induced homopolymerisation. From ^{1}H-NMR analysis before and after 20-min green light irradiation of **1** + **2a** ($CDCl_3$), the [4+2] cycloadduct **3a** was found to be near-quantitatively formed yet traces of the TAD-homopolymer were also detected (see Figure S2 for ^{1}H-NMR analysis). In an attempt to completely suppress this polymeric side product formation – which is strongly solvent-dependent[43-44] – the photoaddition of **1** to **2a** was also studied in acetone-d_6. Whereas again no cycloadduct was observed when the initial TAD-naphthalene mixture was kept in the dark (^{1}H-NMR spectrum, Figure 2b), 45-min irradiation was found to exclusively transform all TAD into the cycloadduct **3a**, along with an untouched excess of the naphthalene substrate (Figure 2c). Thus, competitive photopolymerisation of **1** no longer occurred when the light-driven cycloaddition was carried out in acetone.

Whereas the forward TAD-naphthalene cycloaddition reaction proceeds slower when changing the solvent from chloroform to acetone (i.e. 45 min vs. 20 min), the purple colour originating from released **1** appeared to unfold considerably faster in the dark. This qualitative insight is in line with previously reported cycloreversion rates of isolated **3a** in a range of different solvents, although determined under irreversible TAD-quenching conditions (i.e. in the presence of a co-reactant).[45] Since we here intend to use the thus far unexploited dynamic behaviour of the TAD-naphthalene cycloaddition as an autonomous reversible covalent crosslinking system, the thermal cycloreversion of **3a** needed to be monitored independently. Thus, following quantitative photoconversion of **1** into **3a**, kinetic ^{1}H-NMR measurements were next carried out at 25 °C shielded from ambient light. A first order decrease in **3a** with a half-life time of 9.5 h and an observed rate coefficient $k_{obs}^{25°C}$ of 2.03 10^{-5} s^{-1} was derived from the corresponding cycloreversion profile (Figure 2d). After 60 h, an equilibrium value of 2 % cycloadduct was eventually reached, which corresponds well with the amount of **3a** that is formed in a parallel dark reference experiment (see Figure S3). In other words, once the visible light is switched off, the TAD/naphthalene cycloadduct spontaneously reverts back to yield the initial reagents. Interestingly, the driving force for the spontaneous dissociation can be completely halted, which was demonstrated by the thermal stability of cycloadduct **3a** upon reductive treatment in order to remove the isolated double bond (refer to Figures S4-S5). Hence, the TAD/naphthalene system offers the potential to transform its dynamic behaviour into a permanent covalent linkage when applying a chemical trigger.

Next to the demonstrated light-induced conjugation and subsequent thermal dissociation, a final question that remained unaddressed was whether the covalent nature of the TAD/naphthalene adduct can be stabilised by continuous green light irradiation. This is an important aspect in the design of our targeted TAD/naphthalene-based LSDMs as the network integrity and material properties would hence be preserved throughout the irradiation process. A TAD-trapping experiment was hence devised to determine the amount of covalently bound cycloadduct that remains untouched under continuous irradiation via offline ^{1}H-NMR analysis (refer to Supporting information for a detailed description). Although **3a** was shown to maintain its dynamic behaviour, the equilibrium mixture of the TAD/naphthalene photoreaction remained near-quantitatively populated by the covalently bound cycloadduct over the course of 2 h-irradiation (i.e. > 95 %, Figure S6). Hence, the autonomous TAD/naphthalene crosslinking points that would built up our envisioned LSDMs are expected to be *light-stabilised*.

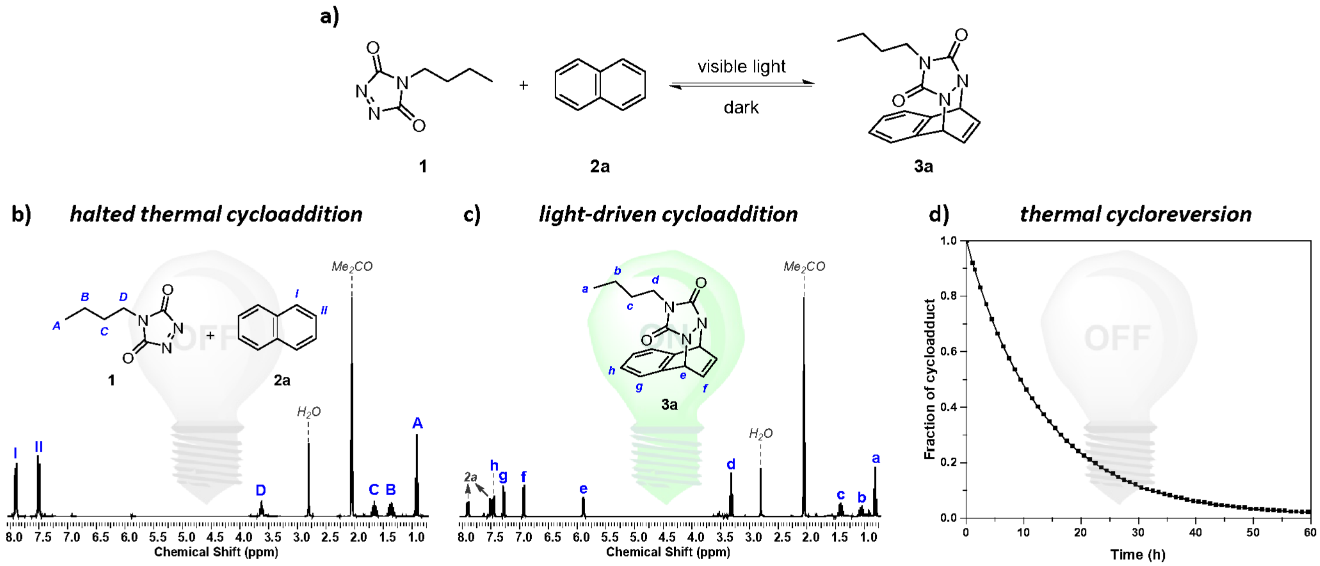
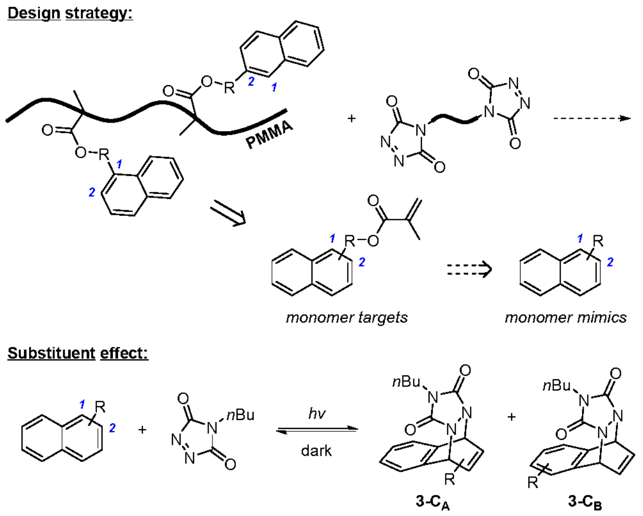


Figure 2. Light-driven dynamic TAD-naphthalene cycloaddition. a) Visible light-induced (λ = 515 – 525 nm, 16 mW cm^{-2}) cycloaddition reaction of 4-*n*-butyl-TAD (**1**, 1.0 eq., 15 mM in $CDCl_3$ or Me_2CO-d_6) in the presence of naphthalene **2a** (1.2 eq.) results in the formation of a thermally labile photoproduct **3a**, which reverts back to the initial substrates upon switching the lights off. b) Whereas no TAD-naphthalene cycloadduct is observed from the ^{1}H-NMR spectrum (Me_2CO-d_6) when **1** + **2** is kept in the dark for 45 min, c) the exclusive and quantitative formation of **3a** is verified by the ^{1}H-NMR spectrum recorded immediately after 45-min green light impact. d) The spontaneous cycloreversion of **3a** in the dark at 25 °C is monitored through kinetic ^{1}H-NMR measurements, carried out immediately after LED irradiation of **1** + **2a** (15 mM, Me_2CO-d_6, λ = 515 – 525 nm, 16 mW cm^{-2}, 45 min).

Macromolecular design. Having identified a fast and stabilised covalent TAD/naphthalene bond formation upon visible light impact in combination with a relatively slow debonding in the dark, we next aimed to introduce the unique light-stabilised dynamic features in a macromolecular context. Because the synthesis of multifunctional TAD compounds is rather challenging,[38, 46] substituted naphthalene derivatives were screened and incorporated into a polymeric matrix, so to develop macroscopic LSDMs (see Scheme 1).

Scheme 1. Design of light-stabilised dynamic materials. Macromolecular implementation of the TAD/naphthalene chemistry into covalent polymer networks by reacting a bisfunctional TAD with a naphthalene-containing prepolymer. The latter can readily be obtained from methacrylate monomers derived from substituted naphthalene building blocks, although different regioisomers can potentially be formed upon TAD-addition.



Introducing substituents onto the naphthalene scaffold, however, can greatly influence TAD-addition and moreover result in the formation of different regioisomers (see Scheme 1, whereby C_A denotes cycloaddition onto the substituted and C_B non-substituted aromatic ring). Hence, the forward light-driven TAD-cycloaddition of selected naphthalene monomer mimics **2b** and **2c** (Figure 3a) was first investigated. While 45-min irradiation of **1** (15 mM, Me_2CO-d_6, green LEDs) in the presence of 1-substituted naphthalene **2b** exclusively afforded cycloaddition onto the non-substituted ring (**3b-C$_B$**), its 2-substituted counterpart **2c** yielded both regioisomers, slightly favouring adduct formation onto the more electron rich ring system (i.e. **3c-C$_A$**:**3c-C$_B$** = 58:42, Figure 3a; refer to Figures S7-S10 for structure elucidation of the investigated cycloadducts).

Having identified the regioselectivity in the forward TAD-cycloaddition, kinetic ^{1}H-NMR measurements were next carried out to also examine the naphthalene substituent effect on the thermal retro-reaction. The resulting cycloreversion profiles indicated a less pronounced dynamic behaviour compared to the plain cycloadduct **3a** with more than 30 % of **3b** and **3c** still detected after 60 h of darkness (Figure 3a). Similar results were obtained upon increasing the alkyl-spacer length on the naphthalene core (refer to Figure S11 for superimposable cycloreversion profiles of the ethyl-substituted counterparts).

The remaining high fraction of covalently bound TAD-naphthalene upon standing in the dark for several days is detrimental for the design of the LSDMs since the light-induced crosslinked materials would refrain from macroscopic reversibility as a result of insufficient debonding. Nonetheless, valuable information was extracted by evaluating the cycloreversion plots of the individual **3c**-regioisomers, for which a 7-fold rate accelerating effect was found for the dissociation of **3c-C$_B$** compared to **3c-C$_A$** (cf. Table S1, with

$k_{obs}^{25°C}$ = 2.23 10^{-5} s^{-1} vs. 0.31 10^{-5} s^{-1}). In fact, the fraction of **3c-C$_B$** almost completely diminished after 30 h.

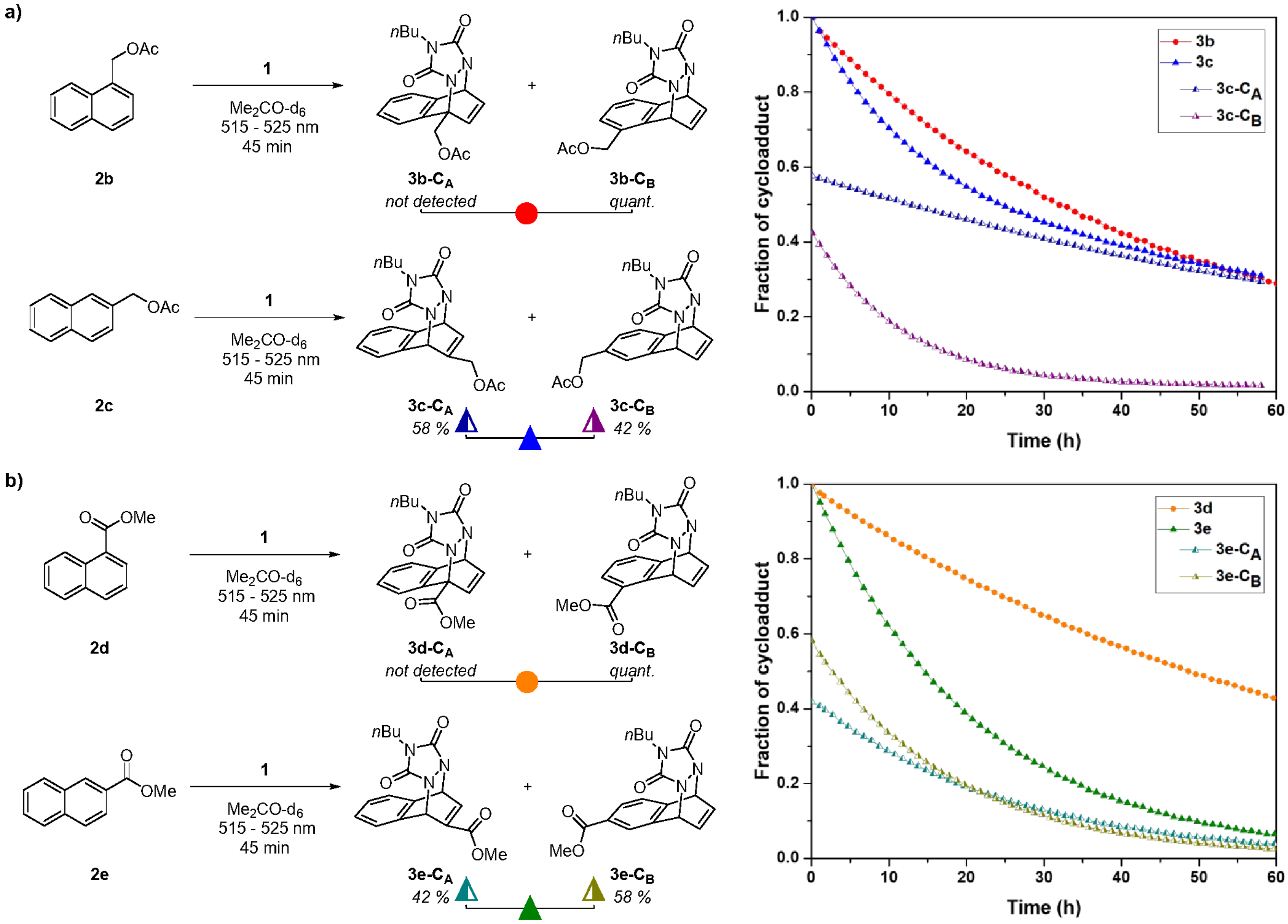


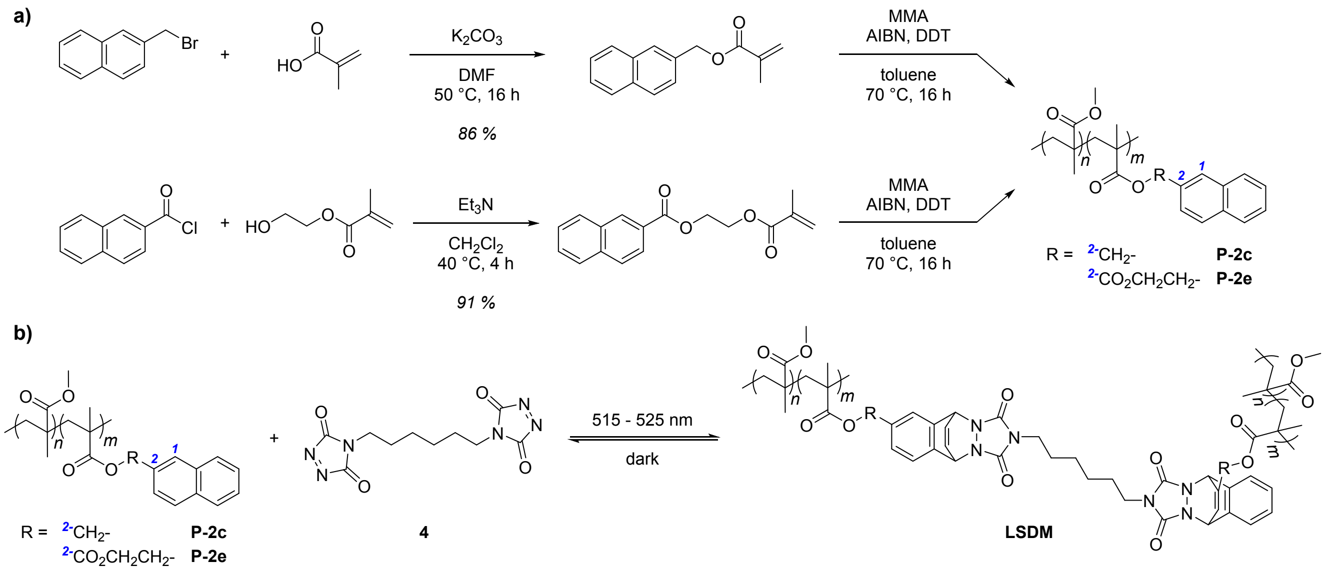
Figure 3. Naphthalene-substitution effect on the TAD-cycloaddition. a) Different regioisomers are obtained during the light-driven cycloaddition of **1** (15 mM, Me$_2$CO-*d$_6$*, λ = 515 - 525 nm, 16 mW cm^{-2}, 45 min) with 1- and 2-alkylated naphthalene monomer mimics **2b** and **2c** (1.2 eq.), respectively. Moreover, the naphthalene-substitution pattern also influences the subsequent cycloreversion kinetics of **3b** and **3c** when the resulting mixtures are placed in the dark (25 °C, Me$_2$CO-*d$_6$*). b) A similar effect is noticed by changing the naphthalene environment to 1- and 2-naphthoate ester monomer mimics **2d** and **2e**, giving a significantly slower or faster thermal cycloreversion (25 °C, Me$_2$CO-*d$_6$*).

Intrigued by this difference in cycloreversion rates, we postulated that directing TAD-addition more towards the non-substituted naphthalene ring would lead to a faster dissociation of the corresponding cycloadducts and thereby anticipate for insufficient debonding in the LSDMs. Thus, naphthoate esters **2d**-**2e** (Figure 3b) were next investigated in an attempt to deactivate the substituted aromatic ring towards cycloaddition. Irradiation of **2d** in the presence of **1** (45 min, green LEDs) again exclusively afforded the substituted cycloadduct **3d-C$_B$**, although the cycloreversion in the dark was much slower compared to its 1-alkyl derivative **3b** (see Figure 3b). In contrast, the non-substituted ring was slightly favoured during the photo-driven addition to **2e** (i.e. **3e-C$_A$**:**3e-C$_B$** = 42:58, Figure 3b), leading to a significant acceleration in overall cycloreversion with only 7 % of **3e** remaining after 60 h (closely resembling the model TAD-naphthalene system **3a**, cf. Figure 2d). The individual regioisomer depletion over time thus validated our strategy to accelerate the spontaneous cycloreversion in the dark, simply by changing the electronic environment of the naphthalene from a methylene substituent to an electron withdrawing ester.

Light-stabilised dynamic materials. With the monomer mimics being evaluated and their distinct cycloreversion rates examined, methacrylate derivatives of the most promising TAD-reactive naphthalene scaffolds were synthesised and incorporated into the side chains of a linear poly(methyl methacrylate) (PMMA, Scheme 2a). Having assessed the photostability of the copolymers upon visible light impact (24 h green LEDs; refer to Figures S12-S13 for NMR and SEC analysis before and after irradiation), their TAD-based photocrosslinking was next screened by subjecting acetone solutions of **P-2c** and **P-2e** in the presence of bisTAD **4** to green LED light (3 mW cm^{-2}, Scheme 2b). Decolouration of the TAD/naphthalene formulations was observed within 1.5 h and crosslinking of both polymers was indicated by a vial inversion test while the network integrity was verified under prolonged irradiation. Following photocuring, the initial purple TAD-colour readily reappeared in both gels when the green light was switched off and the formed networks weakened over time until they eventually collapsed (cf. Figures S14-S15 for NMR and

DSC analysis of the collapsed networks). In agreement with the cycloreversion model studies (cf. Figure 3), the **P-2e**-based material with the naphthalene units attached to the PMMA backbone via an ester functionality was found to collapse faster than its **P-2c** analogue (i.e. 3 h vs. 4 h).

Scheme 2. Synthesis of light-stabilised dynamic materials. a) Preparation of naphthalene-containing poly(methyl metacrylate) P-2c and P-2e, inspired on the previously investigated monomer mimics 2c and 2e, through a free radical copolymerisation of the naphthalene monomers and methyl metacrylate (MMA) with 2,2'-azobis(2-methylpropionitrile) (AIBN) as radical initiator and 1-dodecanethiol (DDT) as chain transfer agent. b) The resulting naphthalene prepolymers are transformed into their corresponding LSDMs through photocuring in the presence of the bisfunctional TAD crosslinker 4 (λ = 515 - 525 nm, 3 mW cm^{-2}, 1.5 h).



Rheological investigations. To verify the postulated LSD properties of the obtained gels, the viscoelastic response of the TAD/naphthalene formulations was monitored through isothermal photorheology measurements under oscillatory shear mode at 25 °C. In contrast to the above photoinduced crosslinking experiments, propylene carbonate instead of acetone was used to prevent solvent evaporation during prolonged measurement times. The curing profiles of the PMMA/TAD solutions, depicted in Figure 4 for **P-2e**/**4** and Figure S16 for **P-2c**/**4**, indicated low initial storage moduli G' (i.e. near the limit of detection) together with low loss moduli G", which remained constant over the course of one hour when kept in the dark (Figure 4a). Irradiation with visible light (λ = 400 – 500 nm, 62 mW cm^{-2}), however, resulted in an abrupt increase in G' with a sol-gel transition observed within 30 min (Figure 4b). After 3 h, the storage modulus reached a plateau (ca. 3 kPa), thereby indicating complete photocuring of the material. Moreover, no deviation in the storage modulus was detected when the samples remained exposed to visible light for an additional 7 h (Figure 4c). Notwithstanding some minor weakening observed for **P-2e**, both cured TAD/naphthalene gels thus retained their crosslinking integrity and were hence stabilised under continued irradiation.

Besides their visible light-stability, the subsequent disintegration of the LSDMs when placed in the dark was also investigated. It should be noted that once the TAD/naphthalene formulation was fully cured, a constant normal force (0.2 N) was imposed onto the gels, which was found critical to prevent erroneous drifts in the storage modulus during lengthy rheology measurements (cf. Figure S17).[47] After the visible light was switched off, a significant decrease in G' was immediately detected, indicating a reduction in crosslinking density and thus loss of the network integrity (Figure 4d).

Essentially, a similar response in viscoelastic behaviour was obtained for both **P-2c**- and **P-2e**-based networks, although the former gave a markedly delayed gel-to-sol transition (i.e. 8.5 h vs. 4.5 h). Such a delayed collapse of the network can directly be related to the nature of the naphthalene substituent and perfectly agrees with the kinetic cycloreversion studies of the respective monomer mimics (cf. Figure 3). Lowering the amount of TAD crosslinker evidently resulted in a less stiff material upon photocuring and much steeper decline in G' as soon as the light was switched off (refer to Figure S18). Eventually, a new plateau in G' and G" was reached that slightly deviated from the initial moduli before photocuring, although this can be attributed to the remaining equilibrium fraction and thus incomplete dissociation of the TAD-naphthalene cycloadducts.

In a final rheology experiment, the photoinduced crosslinking and room temperature triggered decrosslinking was repeated to demonstrate the LSDMs' light-switchability. The reversible formation and dissociation of the TAD-naphthalene crosslinking points was indeed evidenced by several sol-gel transitions during consecutive cycles of 3 h visible light, followed by standing in the dark for another 15 h (see Figure 4e).

Despite the continued light-switchable transitions, a weaker gel yet higher viscous solution was obtained after the second bonding and debonding cycle, which was even more pronounced during a third on/off cycle (cf. Figure S19), thereby indicating a loss of material properties during long-term recyclability. Nonetheless, the visible light-induced crosslinked

LSDMs were shown to be readily and repeatably (i.e. up to 3 times) transformed into a liquified state by placing the TAD/naphthalene cured materials in the dark. Moreover, the thermal covalent debonding times can be effectively tuned, either by lowering the amount of crosslinker or by making slight chemical modulations onto the naphthalene scaffold, which could potentially eliminate long-term recyclability issues in this first generation of LSDMs.

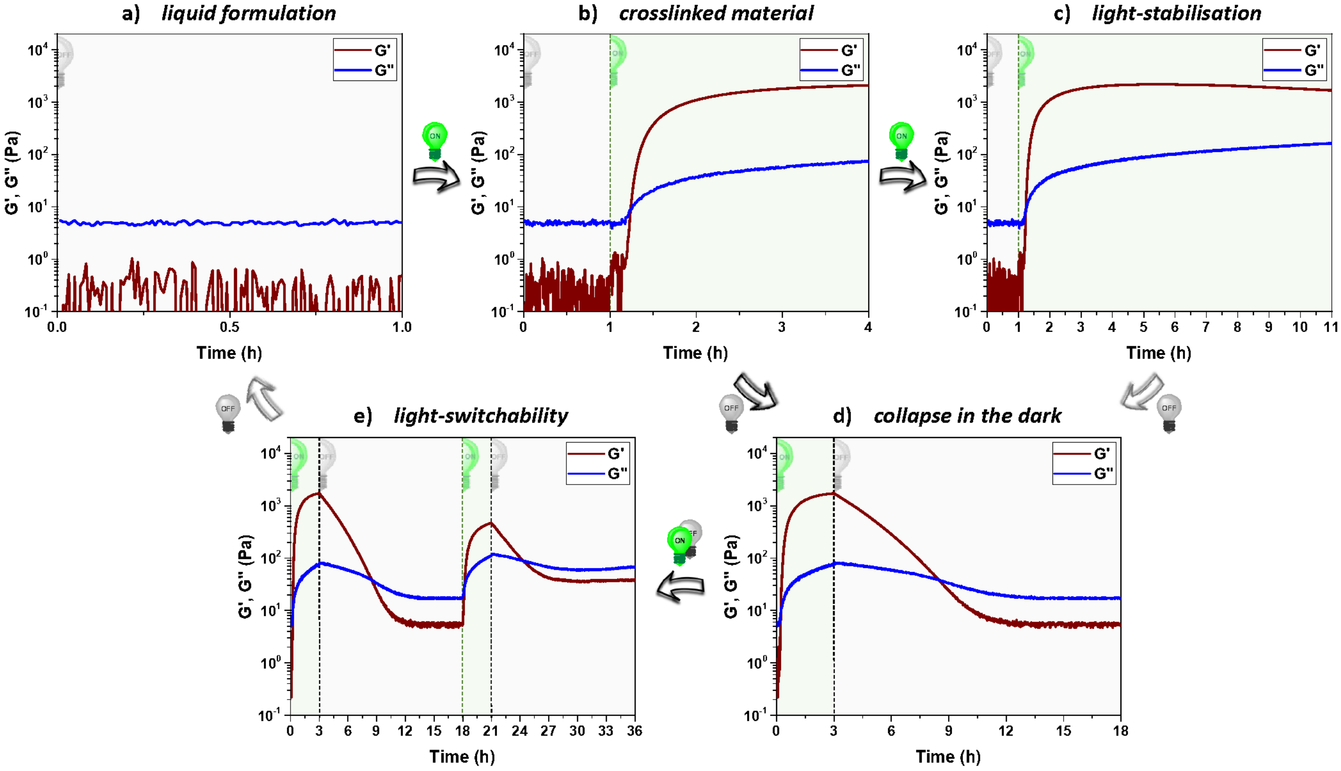


Figure 4. Rheological evaluation of light-stabilised dynamic material **P-2e/4**. a) Whereas the initial liquid formulation of naphthalene-containing polymer **P-2e** (0.21 g mL^{-1} in propylene carbonate) and TAD crosslinker **4** (equimolar amounts of naphthalene to TAD) was shown to be non-reactive when kept in the dark for 1 h, b) a crosslinked material was effectively obtained after 3 h of irradiation (λ = 400 – 500 nm, 62 mW cm^{-2}) as indicated by the response in viscoelastic behaviour. c) Keeping the light switched on for an additional 7 h did not affect the network integrity, evidencing the light-stabilisation of the thus formed covalent polymer network. d) When kept in the dark (at 25 °C), however, a steep decline of the material's stiffness was detected over time, which illustrates the dissociation of the crosslinking points through the spontaneous TAD-naphthalene cycloreversion. e) Finally, the bonding/debonding process can be re-initiated by consecutive periods of visible light (3 h) and darkness (15 h).

Visual demonstration of LSDM behaviour. Besides rheology measurements, the retention of crosslinking under continuous irradiation and subsequently triggered decrosslinking or debonding by switching the lights off was also visually demonstrated. Specifically, a propylene carbonate solution of the most thermally labile TAD-reactive naphthalene-containing polymer **P-2e** was first transformed into a network upon photocuring with **4**. A firm colourless material was retrieved from a square mould after 5-h green light irradiation (see Figure 5-I), after which a faint purple colour was rapidly reinstated. The cured sample was subsequently placed onto a metal support grid and exposed to an additional 5 h of green light (Figure 5-II). The material showed an identical appearance compared to the pristine sample, demonstrating the retention of the crosslinked integrity and therefore the light-stabilised nature of the TAD/naphthalene-based material (Figure 5-III).

When the LSDM was subsequently placed in the dark, decrosslinking was illustrated by the regeneration of a deep purple colour within 2 h (Figure 5-IV) and more clearly by the dripping formulation and migration of the material through the metal support grid over time (Figure 5-V and VI). The collapse of the network continued until a red solution was eventually recovered 40 h after the green light was switched off (Figure 5-VII). In addition to demonstrating the light-stabilisation and dark collapse, the resulting polymer solution was finally reused in a series of macroscopic shape transformations (refer to Figure S20), thereby illustrating the light-switchable sol-gel transition of the TAD/naphthalene materials.

CONCLUSION

We introduced an unprecedented dynamic polymer system that can be reversibly switched between two states of matter, i.e. from a covalently crosslinked material into a viscoelastic liquid and back, using only one colour of light. We deliberately sought for a single photochemically triggered crosslinking chemistry that can induce network formation under visible light, keep the resulting material stable whilst irradiated, and finally allow it to collapse through covalent dissociation by simply switching the light off.

Here, the visible light-driven cycloaddition of TADs to naphthalenes was evaluated to possess such unique dynamic covalent behaviour. Following their macromolecular implementation through the design of appropriate naphthalene-containing monomers, photocuring with a bisfunctional TAD crosslinker led us to prepare the so-called *light-stabilised* *dynamic materials (LSDMs)*. The resulting visible light-controlled dynamic behaviour was assessed by means of rheology measurements while the transformation from a crosslinked structure under irradiation into a liquefied viscoelastic material in the dark was also visually demonstrated.

In addition, bonding-and-debonding cycles could be repeatably accessed, as illustrated by consecutive shape transformations. Moreover, the thermal cycloreversion kinetics of the TAD-naphthalene adducts can also be tuned on the material level by making small alterations to the naphthalene chemical environment.

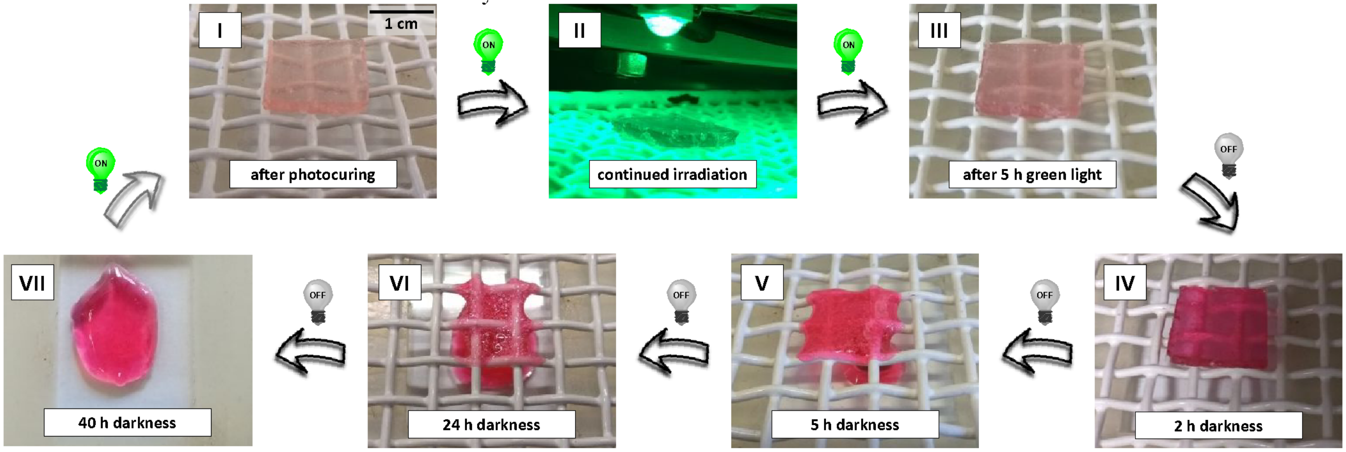


Figure 5. Macroscopic demonstration of light-stabilised dynamic behaviour. After curing a propylene carbonate solution of naphthalene-containing polymer **P-2e** (0.84 g mL^{-1}) and bisTAD **4** (in equimolar TAD vs. naphthalene amounts) with green light (λ = 515 – 525 nm, 3 mW cm^{-2}, 5 h, panel I), the obtained crosslinked material is placed onto a metal support grid and irradiated for an additional 5 h (II) without affecting the network integrity (III). A deep red colour is reinstated upon switching the lights off (III -> IV) and the decrosslinking process leads to a liquefied material that drips and eventually migrates through the grid (V -> VI). After 40 h of darkness, a clear purple solution is eventually recovered (VII) that can be subsequently cured again upon irradiation.

The TAD/naphthalene-based LSDMs described herein constitute a pioneering example to introduce an unparalleled dynamic covalent behaviour in light-directed applications – ranging from optical devices to cell scaffold engineering and 3D photoresist design – enabling on demand debonding under the mildest trigger of all: darkness.

ASSOCIATED CONTENT

Supporting Information.

Materials and instrumentation (including spectral details of emission sources), supplementary figures and tables, experimental and synthetic procedures and supplementary NMR spectra.

This material is available free of charge via the Internet at http://pubs.acs.org.

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ABBREVIATIONS

AIBN, 2,2'-azobis(2-methylpropionitrile); DDT, 1-dodecanethiol; DSC, differential scanning calorimetry; LED, light-emitting diode; LSD, light-stabilised dynamic; LSDM, light-stabilised dynamic material; MMA, methyl methacrylate; NMR, nuclear magnetic resonance; PMMA, poly(methyl methacrylate); SEC, size exclusion chromatography; TAD, 1,2,4-triazoline-3,5-dione.

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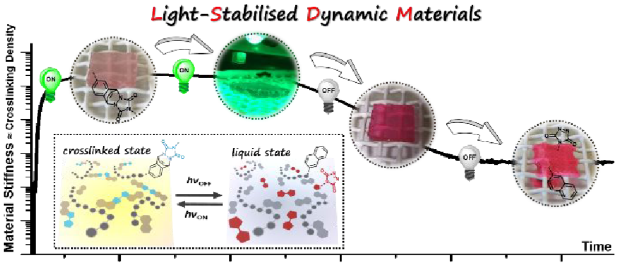

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