

# Combined Photopolymerization and Localized Photochromism Generation by Aza-Diarylethene and Hemiindigo Synergy

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## Abstract

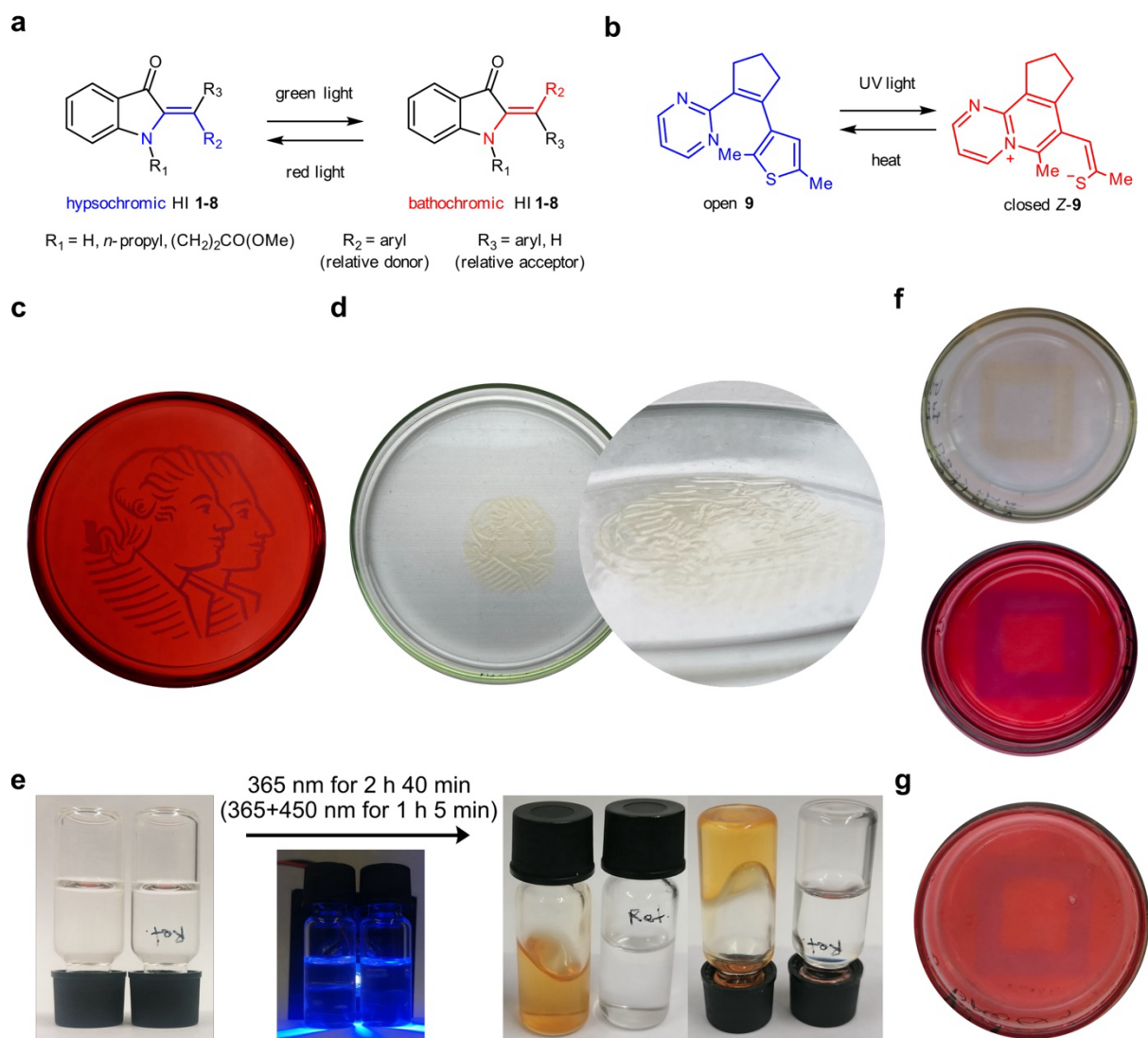
**Molecular photoswitches produce light-controlled changes at the nanometer scale and can therefore be used to alter states and behavior of materials in a truly bottom-up fashion. Here we show an escalating photonic complexity of material property control with light using a recently developed aza-diarylethene in combination with hemiindigo (HI) photoswitches. First, the aza-diarylethene can be used as a photoswitch in polystyrene (PS) and to inscribe relief-type 3D structures reversibly into PS. Second, aza-diarylethene can further be used as a photoinitiator for light-induced polymerization of acrylates, demonstrating for the first time light-controlled chemical reactivity control with its zwitterionic switching state. Third, aza-diarylethene and HIs are implemented into aza-diarylethene polymerized PMA, generating photochromic polymers. At the fourth level, the binary mixture allows to synergize aza-diarylethene induced photopolymerization with localized photochromism changes of the simultaneously entrapped functional HI. With such multi-level light response, the utility of this particular photoswitch combination for applications in advanced photonic materials is demonstrated.**

## Introduction

Applications of molecular photoswitches<sup>1, 2</sup> in materials are of high interest because multiple properties can be controlled with nanoscale precision by simple outside light irradiation stimuli.<sup>3-11</sup> Consequentially, the resulting light-responsive materials give rise to smart and programmable behavior, the potential of which is just starting to be tapped. A very potent yet simple approach in this regard is implementation of photoswitches into transparent polymers,

endowing the latter with photochromism.<sup>12, 13</sup> This allows for reversible inscription of information with light and resulting applicability in optical memories, cryptography, displays, or programmable filters.<sup>14-17</sup> When geometrical or electronic changes of the molecular photoswitches are leading to corresponding changes within the embedding material, light-control over its shape, density, aggregation state, or wettability (to name a few options) can be achieved.<sup>7, 18-23</sup> There are virtually limitless applications that result in such cases including soft robotics,<sup>24-26</sup> haptic topological material changes,<sup>27, 28</sup> or self-healing.<sup>29-31</sup> Photoswitches can further be used as molecular photoinitiators for polymerization and thus open up applications in 3D-printing,<sup>32-37</sup> for 4D materials with dynamically controllable changes,<sup>6, 38</sup> or for sequence-precise information polymers<sup>39</sup> (again to just name a few). In the overwhelming cases most common photoswitches are used for materials application, i.e. azobenzenes,<sup>40-42</sup> diarylethenes,<sup>43</sup> spiropyranes,<sup>44, 45</sup> or stilbenes.<sup>46, 47</sup> The latter are interesting for materials application in their own right in the more elaborate form of molecular machines.<sup>48-50</sup>

In this work we explore two very recent additions to the realm of photoswitches, hemiindigo (HI)<sup>51-54</sup> (derivatives **1-8**, Figure 1a) and aza-diarylethene **9**<sup>55</sup> (Figure 1b), for their potential in advanced light-responsive materials. HIs belong to the emerging class of indigoid photoswitches,<sup>56-59</sup> which show excellent switching properties, high thermal stability, and broadly tunable absorptions in the visible,<sup>60-65</sup> red,<sup>51, 54, 66-70</sup> and near infrared<sup>71, 72</sup> part of the electromagnetic spectrum. Aza-diarylethene **9** is a heterocyclic variant of diarylethenes and allows to reversibly form a CN double bond photochemically under zwitterion formation and aromatization.<sup>55</sup> We now scrutinized a variety of different applications, starting with photochromic polymers (Figure 1c) and 3D-reversible relief photoimprinting (Figure 1d) before turning to light-induced radical polymerization initiation (Figure 1e), using the resulting polymers to generate photochromic polymers by addition of compounds **1-7**, and **9** (Figure 1f), and finally synergizing photocontrolled polymerization and localized photochromism simultaneously (Figure 1g).



**Figure 1** Five levels of light-controlled material changes using HIs **1-8** and aza-diarylethene **9**. **a** Schematic overview of HI **1-8** switching modes. **b** Schematic overview of aza-diarylethene **9** switching modes. **c** Photochromic transparent PS polymer using HI **8** as light-responsive component. The FAU University Seal was inscribed by using a photomask. **d** 3D-relief photoimprinting in PS using aza-diarylethene **9** as light-responsive component. The FAU University Seal was inscribed using a photomask. **e** Photopolymerization of MA using aza-diarylethene **9** as photoinitiator in MA. Irradiation of a 2.8 mM solution of **9** in MA with 365 nm (260 mW) leads to polymerization within 2 h 40 min, irradiation with 365 nm (260 mW) + 450 nm (400 mW) leads to polymerization within 1 h 5 min. The reference sample contains solely MA and does not polymerize under the same conditions. **f** Photochromic transparent PMA polymer initiated with aza-diarylethene **9** and mixed with aza diarylethene **9** (top) and HI **7** (bottom) after polymerization. **g** Synergized photopolymerization by **9** in the presence of unaffected HI **7** and localization of HI **7** photochromism in the resulting

MA-polymer. The petri dishes in c and d have a diameter of 80 mm, the petri dishes in f and g of 30 mm.

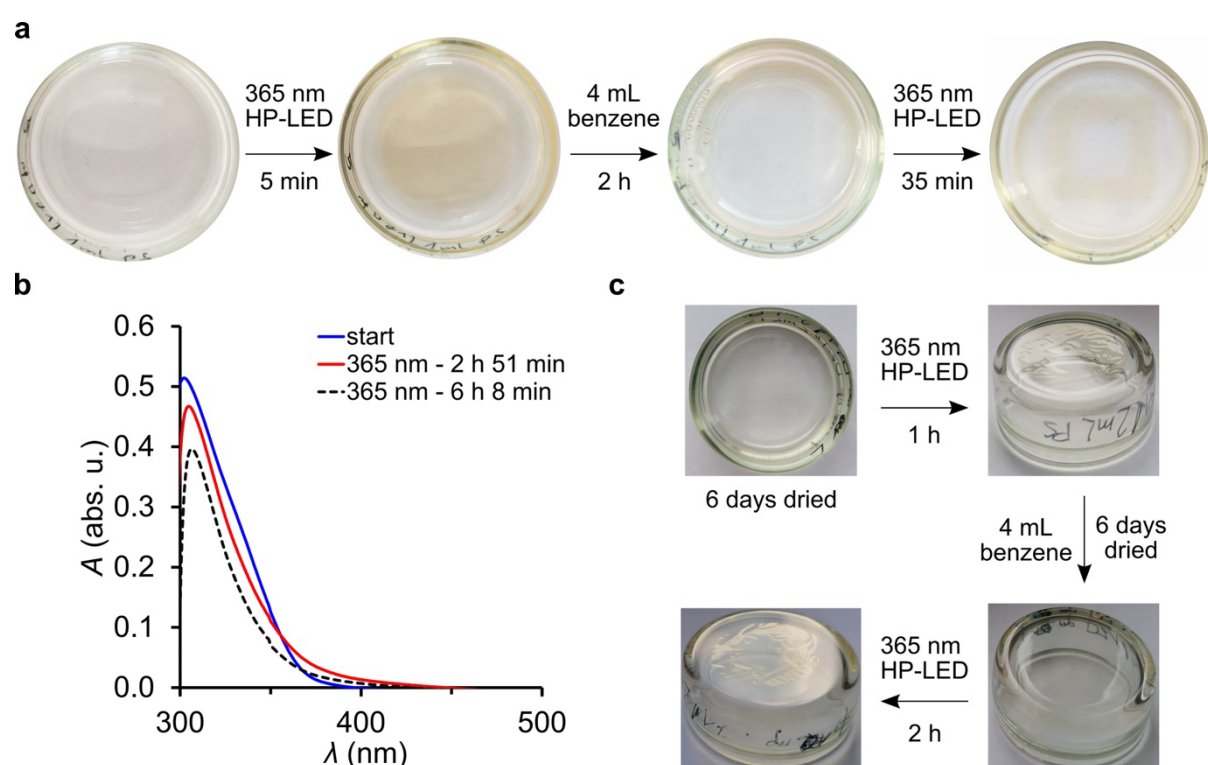
## Results and discussion

### Photoswitching of aza-diarylethene **9** in PS

Recently, we have reported compound **9** undergoing a reversible electrocyclic ring closure mechanism with concomitant C-S bond cleavage leading to a charged zwitterionic species by UV light irradiation (Figure 1b). In this work we turned our attention to aza-diarylethene **9** and its photoresponse in a polymer context. First, **9** was embedded into polystyrene (PS) and also in this case reversible photoresponse with light of 365 nm is observed allowing to localize photoswitching and inscribe information into the material (Figure 1d, Figure 2a). Moderate color contrasts are observed as a result of the photoswitching from open **9** to closed *Z*-**9**, which allows to distinguish the inscription with the naked eye. Upon diluting the inscribed polymer with benzene at ambient temperature, the inscription can be erased and a transparent colorless material is received again upon drying. Another round of photoinscription directly showed reversible photoswitching of **9** in polystyrene (Figure 2a). From the corresponding UV/Vis spectroscopic analysis of **9** photoswitching in PS (Figure 2b) we observed that enrichment of closed *Z*-**9** as well as the charge separation of the zwitterionic state are less pronounced compared to MeOH solution, which explains the smaller color contrast in the polymer. In MeOH solution, closed *Z*-**9** can further undergo light-induced *Z/E* photoisomerization upon longer light irradiation durations with light of 365 nm to an extent of up to 3%, which leads to a diminishing of the yellow color and corresponding lower intensity of the visible absorption band in the UV/vis spectrum. Further accumulation of the closed *E*-**9** isomer is possible through several irradiation cycles at ambient temperature. Given the only pale-yellow color observed upon photoswitching of **9** in PS and the incomplete recovery of the colorless open **9** form after dilution, we assign the resulting photoproducts in PS to contain a noticeable contribution of the thermally more stable ring closed *E*-**9** isomer.

A very interesting behavior is observed upon irradiation of **9** using a photomask of very narrow inscription lines in PS, which leads to a persistent 3D-relief formation in the irradiated areas (Figure 1d and 2c). The specific molecular cause for this behavior is currently under investigation in our laboratory, but a strong local accumulation of charged ring closed **9** species and concomitant localized polymer adjustments and packing changes seem likely to be important. Evidence for the presence of charged **9** isomers is directly obtained from the localized color changes, which coincide with the 3D structured polymer areas. Such behavior

can be used to inscribe information in a haptic way instead of relying on optical changes, which is of potential interest for applications in braille displays, or reprogrammable stamps, for example. After diluting the material with benzene and allowing the chromophore to thermally isomerize to the open **9** form at ambient temperature, the imprint is erased and a smooth surface is obtained into which a different 3D-relief can be inscribed again (Figure 2c). With this series of experiments reversibility of the 3D inscription process is demonstrated a unique application area for aza-diarylethene photoswitches.



**Figure 2** Localized light responses in photochromic and haptic polystyrene polymers inheriting aza-diarylethene photoswitch **9**. **a** Photochromic polymer with **9** in PS showing reversible writing and erasing. **b** Photoswitching of open **9** to closed **Z-9** in PS. **c** Reversible photoinduced 3D-relief formation upon photoswitching of **9**. The FAU University Seal was inscribed in a haptic way using a photomask.

### Photoinduced Polymerization of MA by aza-diarylethene **9**

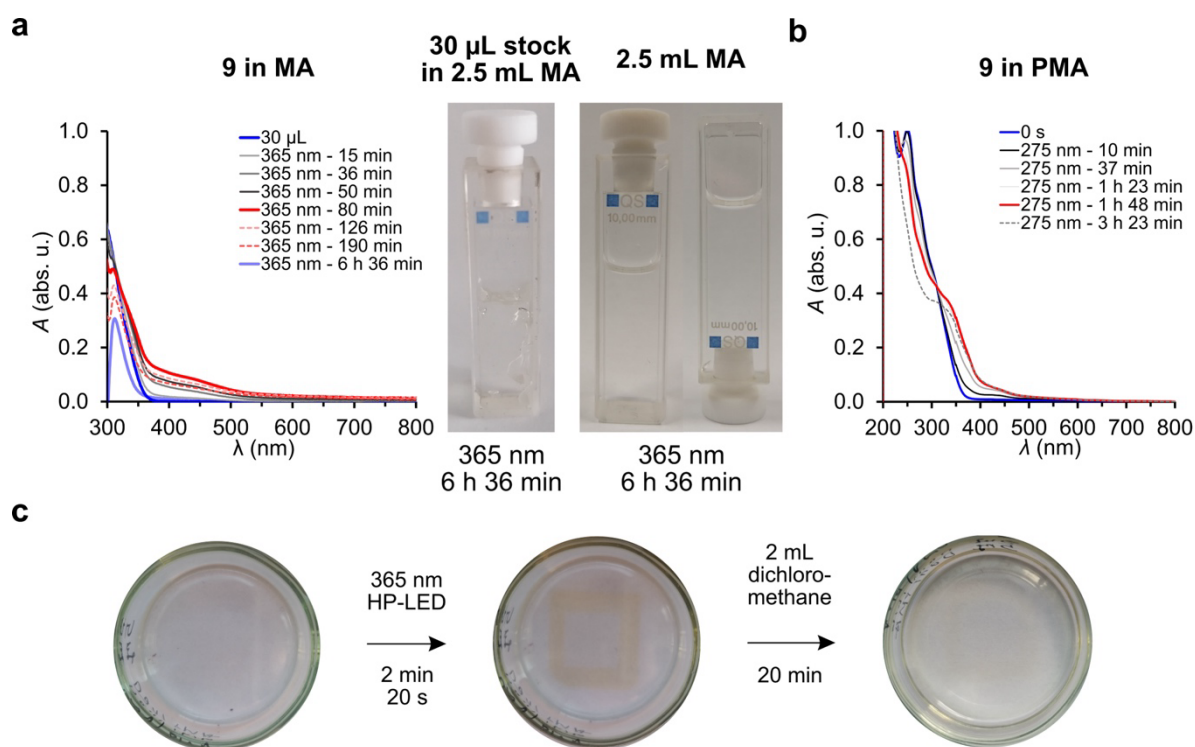
As described above, photoswitching of aza-diarylethene **9** induces formation of an aromatized zwitterionic state. This zwitterion inherits a positively charged pyrido[1,2-a]pyrimidin-5-ium ring and also a highly nucleophilic thiolate functional group (Figure 1b). Light irradiation thus leads to formation of a pronounced chemical reactivity and we were wondering if starting from the zwitterionic form we could generate radicals initiating radical polymerization upon

continued light irradiation similar to zwitterionic merocyanines.<sup>32, 73-75</sup> In this way, light could be used as an external trigger ultimately controlling formation of a solid material in a timed fashion. We projected that photoswitching of **9** would first lead to formation of the thiolate, which would then form radicals and be able to initialize radical methyl acrylate (MA) polymerization by initial attack on the MA Michael system. The resulting radicals would then polymerize the material under continuous carbon-carbon bond formation. We tested different mixtures of aza-diarylethene **9** and MA and found suitable conditions in the range between 0.4 - 13 mg of **9**/mL MA and irradiation times with light of 365 nm (260 mW) or 367 nm (1 W) of under 4 h. Those mixtures remain liquid in the absence of light without any noticeable polymerization happening. To our delight, irradiation with 365 nm light did in fact induce polymerization e.g. within 2 h 40 min at a concentration of 0.7 mg **9**/mL MA and a solid yellow material was obtained as a result (Figure 1e). The same irradiation conditions in the absence of **9** did not lead to any visible polymerization and only liquid MA monomers remained. Only much longer light irradiation duration of more than 17 h with 365 nm (260 mW) did ultimately result in radical polymerization of MA (see Supporting Figure 16). Additionally, we wanted to understand if the polymerization initiating event was triggered by the excited state of open **9** or by the excited state of closed *Z*-**9**. We therefore irradiated a sample containing 0.7 mg **9**/mL MA simultaneously with light of 365 (260 mW) nm and 450 nm (400 mW). Full polymerization occurred within 1 h 5 min (Supporting Figure 19). The polymerization speed thus was more than doubled compared to irradiation with solely 365 nm light. As open **9** does not absorb at 450 nm, and closed *Z*-**9** absorbs both at 365 nm and 450 nm, we therefore assume the polymerization event being triggered by the photoproduct of **9**, the closed *Z*-**9** isomer. If going to concentrations above 13 mg **9**/mL MA or below 0.4 mg **9**/mL MA no polymerization occurred in under 4 h of light irradiation with 365 nm or 367 nm most likely because of radical self-/quenching effects. To prove the radical polymerization mechanism, an equimolar amount of 2,2,6,6-tetramethyl(piperidin-1-yl)oxyl (TEMPO, 0.4 mg/mL) was added to a solution of **9** (0.7 mg/mL) in M and the mixture was irradiated for 2 h 40 min with light of 365 nm (260 mW) (Supporting Figure 18). TEMPO is a literature known radical quencher stopping radical polymerization of acrylic acids. Indeed, in the presence of TEMPO no polymerization occurred, proving the radical polymerization mechanism photoinitiated by **9**. Further, NMR and UV/vis experiments directly revealed the consumption of closed *Z*-**9** resulting in a reduced amount of open **9** after finishing the polymerization process (Figure 3a, Supporting Figures 20-23). In this specific photopolymerization application, aza-diarylethene **9** was thus established

as a viable molecular photoinitiator demonstrating for the first time direct and chemical use of the photoproducts of **9**.

### **Photoswitching of aza-diarylethene **9** within PMA**

We further elevated the polymeric application of aza-diarylethene **9** by using it in two different capacities for the same material. First, MA was polymerized with **9** as photoinitiator in lower concentrations to yield almost colorless, transparent poly-(methyl)-acrylate (PMA). Second, after finishing the polymerization, **9** was added anew to the material as a photochromic component. When analyzing the corresponding UV/vis changes in the transparent material, a somewhat similar behavior to polar protic MeOH solution<sup>55</sup> is observed. In MeOH, **9** undergoes a concomitant ring closure, aromatization, and charge separating zwitterion formation upon irradiation. The resulting closed isomer *Z*-**9** is colored yellow with significant absorption increase in the visible region around 450 nm. In this PMA application, the UV/Vis spectra revealed photoisomerization after irradiating the sample with light of 275 nm similar to the experiments in solution (Figure 3b). Also a broad absorption band appeared around 450 nm indicating the zwitterionic species, which was also visible by the light yellow color change (Figure 3c). The zwitterionic state is more pronounced in PMA (Figure 3b), than it is in PS (Figure 2b) which can be explained by the polarity and rigidity difference of the two polymers. Photodegradation appeared only after irradiation durations between 1 h 48 min and 3 h 23 min with energy rich 275 nm light. The reversibility of this T-type aza-diarylethene **9** photoswitch in PMA was proven by dilution experiments with CH<sub>2</sub>Cl<sub>2</sub>, followed by evaporating the solvent, and monitoring the decolorization to almost colorless again (Figure 3c).



**Figure 3** Light induced polymerization of MA by irradiating compound **9** and localized light responses in photochromic PMA polymers inheriting aza-diarylethene photoswitch **9**. **a** UV/Vis spectra showing irradiation of open **9** (blue) with light of 365 nm leads to closed **Z-9** generation (gray to red) followed by consumption of closed **Z-9** (red dotted) in the course of the polymerization progress until full polymerization occurred and only remaining open **9** (light blue) is visible. The related UV/Vis cuvette is also depicted, as well as a reference cuvette containing only MA after irradiation with light of 365 nm for 6 h 36 min. **b** Photoswitching of open **9** (blue) to closed **Z-9** (black to red) in PMA with light of 275 nm until 1 h 48 min. After 3 h 23 min photodegradation occurred (gray dotted). **c** Reversible T-type photoswitching with light of 365 nm from open **9** to closed **Z-9** (yellow square) and back to open **9** after addition of  $\text{CH}_2\text{Cl}_2$  in PMA at 23  $^\circ\text{C}$ .

### Photoswitching of HIs in PMA

We have recently reported on photochromic PS polymers using newly developed diaryl-HI photoswitches (Figure 1a) as the light-active component. We could demonstrate that their photochromism generating reversible *E/Z* photoisomerization can be retained in the solid material through different external stimuli such as light and acid, giving rise to marked contrast changes between red and purple (Figure 1c). To evaluate the robustness of HIs in different polymers as well as to generally broaden applicability of HIs in polymer applications, we now combined their pronounced photochromism with the photoinitiator functions of aza-

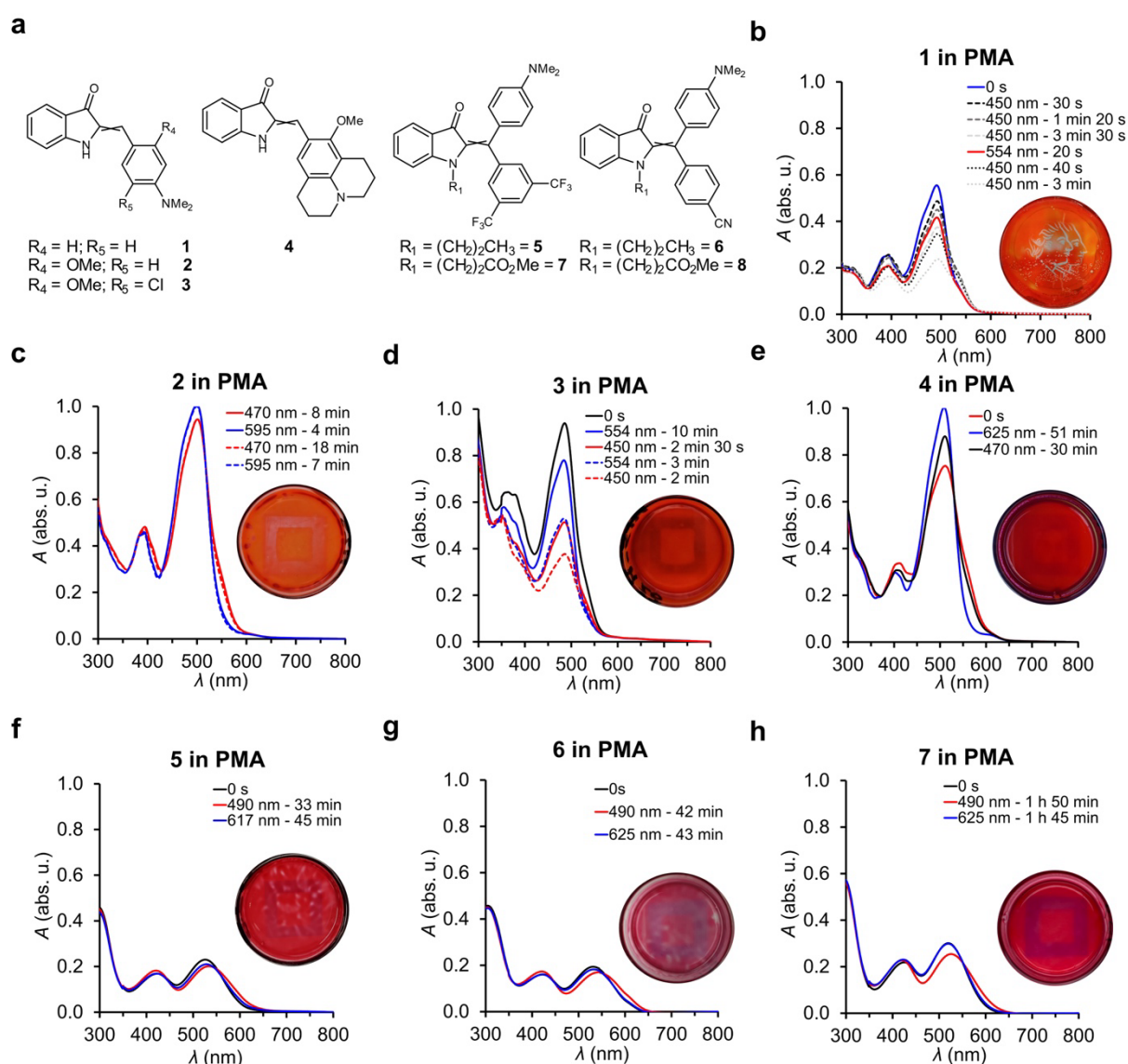


diarylethene **9**. At the first level we introduced the series of HIs **1-7** (Figure 4a) into PMA, which was separately photopolymerized by aza-diarylethene **9** before. To this end the photoinitiated polymerized PMA was diluted in CH<sub>2</sub>Cl<sub>2</sub>, mixed with HIs **1-7**, and subsequently the solvent was evaporated, leading to highly colored and transparent photochromic materials. The photoswitching within the transparent polymers could be followed directly by the naked eye as well as with UV/vis spectroscopy and compared to solution behavior (see Supporting Figures 29-50). When investigating the different derivatives **1-7**, marked differences could be observed depending on the molecular setups as visible by the UV/vis spectra and corresponding photochromic polymers (Figure 4b-h).

Mono-arylated HIs such as **1** are strongly photochromic in solution with maxima separation between the two switching isomers reaching more than 30 nm in monomeric MA. However, within the polymer matrix, the photochromism is markedly reduced, and photodegradation occurs soon after light irradiation (Fig 3b). HI derivative **2** inheriting increasing electron donation at the stilbene-fragment does not deliver a significantly better absorption band separation between the *E/Z* isomers (Fig 3c) but no photodegradation is visible from the spectra. However, visible color paling in the PMA material still indicates photodegradation after prolonged irradiation durations with light of 470 nm. For HI derivative **3** (Figure 3d), which differs from compound **2** by a chlorine substituent in *ortho*-position to the dimethylaniline and *para*-position to the methoxy substituents, again photodegradation occurs soon after irradiating the samples. Irradiating the very electron rich julolidine substituted HI **4** did not lead to photodegradation, but again color differences are not very pronounced (Fig 3e). From analyzing the different UV/vis measurements of compounds **1-4**, some conclusions can be drawn. It is evident that by moving from solution to polymer, a spectral broadening for the individual *E* and *Z* isomers results in an increased spectral overlap. This leads to a reduced addressability of the hypsochromic isomers. In case of the bathochromic isomers, the absorption flanks in the redshifted spectral area are still separated enough, preserving the addressability of the bathochromic isomers similar to that in solution. This effect is the reason for the reduced photochromism achievable in polymers. On the other side, photodegradation effects are drastically increased by moving monoaryl-HIs from solvent to PMA polymer.

Diaryl-HIs are more redshifted than monoaryl-HIs and deliver strong photochromism, pronounced color contrasts between the isomers, and pronounced band separation. Additionally, the second aryl substituent at the stilbene fragment and substitution of the indoxyl-nitrogen lead to photoswitches that are highly robust against photodegradation in solution and in polymer applications.

When employing diary-HIs **4-7** as photochromic components in PMA, robust photoswitching is seen in all cases. Their inherent pronounced photochromism and larger absorption band separation translates favorably into the PMA matrix. In these cases, the very good color contrasts between red and purple remain, allowing to reversibly inscribe information with robust performance into the transparent material (Figure 3f-h). The best visible performance was given by diaryl-HI **7**, which delivered easily distinguishable contrast between deep red and purple as exemplified in Figure 3h. Reversibility was demonstrated by erasing inscribed information with red light and rewriting new information with green light irradiation (Supporting Figure 51).

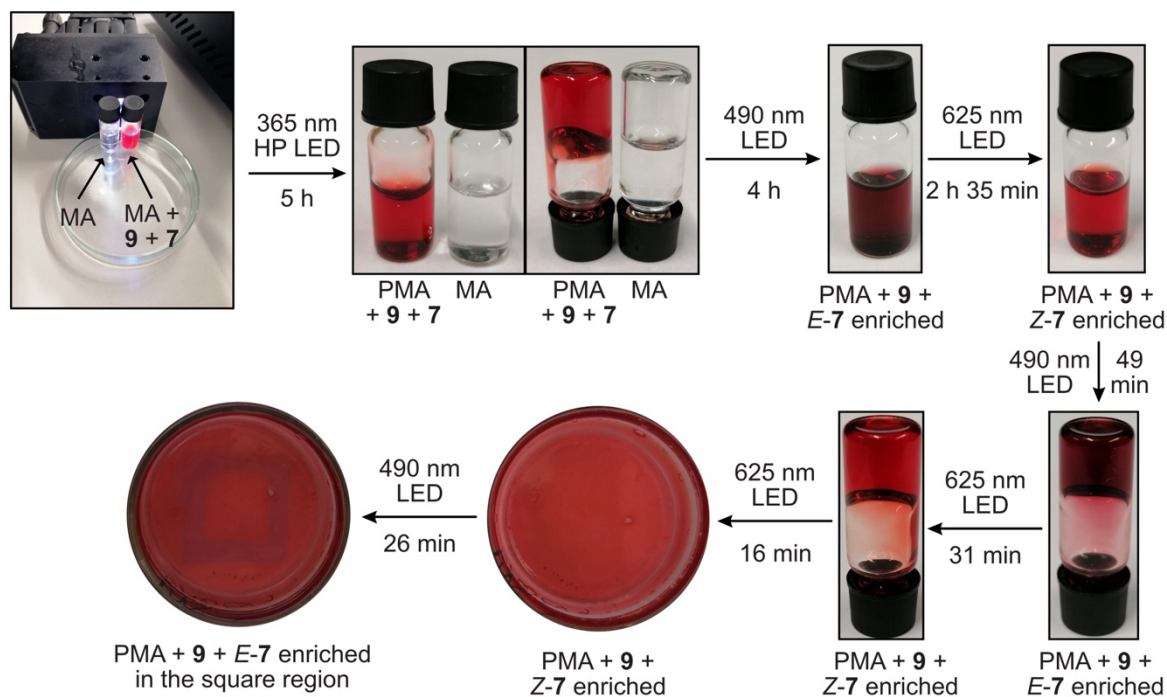


**Figure 4** UV/Vis spectroscopic monitoring of the localized light responses of HI photoswitches **1-7** within photochromic PMA polymers and corresponding petri dishes with photochromic PMA/HI polymers. The inner squares within the petri dishes contain enriched bathochromic isomers, while the surrounding contain the hypsochromic

isomers. **a** Schematic representations of the molecular structures of HIs **1-7** used for the PMA application. **b** Photochromic polymer with HI **1**. **c** Photochromic polymer with HI **2**. **d** Photochromic polymer with HI **3**. **e** Photochromic polymer with HI **4**. **f** Photochromic polymer with HI **5**. **g** Photochromic polymer with HI **6**. **h** Photochromic polymer with HI **7**.

### **Synergistic polymerization of MA by aza-diarylethene **9** in the presence of HI**

Finally, we strived for a synergistic combination of our photoresponsive molecular tools within the same advanced material by using them simultaneously during different light-controlled processes. For this purpose we combined HI **7** and aza-diarylethene **9** in a mixture with MA monomers (m/m  $1 : 1.6 : 1.6 = 7 : 9 : \text{MA}$ ). This mixture remains liquid in the absence of light but can be photopolymerized upon 365 nm irradiation to form a transparent yet strongly red colored solid material (Figure 5). The remaining and unchanged red color directly shows that 365 nm irradiation, zwitterion formation of **9**, as well as the polymerization reactions do not interfere with the HI **7** photoswitch, effectively uncoupling the aza-diarylethene photoresponsive function from the HI function. Interestingly, HI **7** is not destroyed in the presence of a radical polymerization, which is clearly in line with the robustness of indoxyl nitrogen substituted diaryl-hemiindigos. After successful polymerization, the sample was two times irradiated with light of 490 nm and 625 nm demonstrating the retained photoswitchability, before the red solid material was transferred into a flat petri dish and irradiated again with red and green light through a photomask. With the longer wavelength light the photoswitching function of HI **7** was addressed, leading to well visible photochromism and corresponding contrast changes with spatial resolution. Taken together, this multi-photon response establishes a highly advantageous synergistic use of two photoswitches for vastly different purposes within the same smart material application. The first light-responsive component (aza-diarylethene **9**) solidifies the material upon UV light irradiation and in the course of this polymerization traps the second light-responsive component (HI photoswitch **7**) locally by inhibiting its diffusion. As a result, the HI photoswitch **7** can then be addressed with spatial resolution, leading to the possibility of reversible information inscription and erasure with visible and red light. Specific and non-interfering molecular photoresponses are thus creating a multi-photoresponsive material application in which light-induced chemical reactions and reversible photoswitching are synergized.



**Figure 5** Light-triggered MA polymerization using aza-diarylethene **9** as photoinitiator with synergistic interplay of HI **7** in a multi-photoresponsive materials application. Upon 365 nm irradiation, **9** undergoes zwitterion formation. Prolonged irradiation unleashes radical formation that initiates MA polymerization via initial attack of the Michael system. HI **7** is not affected during this polymerization process and stays fully functional proving its exceptional robustness. Reversible visible light photoswitching with 490 nm and 625 nm of **7** in the resulting polymer allows to inscribe and erase information afterwards for several times.

## Conclusion

In summary, we establish here advanced photoresponsive materials with escalating levels of complexity. First, we established transparent light responsive photochromic materials where a single photoswitch component is reversibly alternated to inscribe and erase information covering the UV and visible range of the electromagnetic spectrum. Second, the localized photoswitching of aza-diarylethene **9** was used to reversibly inscribe 3D-relief type structures into the polymers, which broadens applicability of molecular light-responsiveness to include haptic material changes. Third, the capacity for photoinduced radical polymerization initiated by light irradiation of aza-diarylethene **9** was harnessed for the first time. In this way, solidification of a monomeric liquid could be brought under light control in a timed fashion by aid of a novel molecular photoinitiator. Fourth, HIs were mixed with this newly photoinitiated PMA to generate smart polymers that are rich in color contrasts, retaining sufficient

photochromism, are robust against light irradiation and stay intact within the PMA polymer matrix. The photoinitiator function of **9** was then finally synergized with the reversible photochromism changes of HI **7** to obtain a multi-level simultaneous photoresponsive materials application. Here both light-responsive components work together to enable full photocontrol over solidification, localization of the photoresponse, and reversible information inscription into the resulting material. With these results we establish a new way for integrating different elements of photocontrol into a smart material application allowing to time and localize specific responses to light irradiation. Further studies to refine and enhance photocontrol are currently ongoing in our laboratories.

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**Keywords:** photochromism • hemiindigo • aza-diarylethene • light-responsive materials • photopolymerisation

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TOC Figure

