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**PAPER**

# Photo-induced molecular alignment of trisazobenzene derivatives

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Optically active small-molecular trisazobenzene derivatives are explored that allow facile photo-induced fabrication of holographic volume gratings which are unusually stable over time compared to structures based on other small-molecular organic compounds. The origin of this favorable characteristic of such architectures is investigated with three compounds that structurally differ only in the length of an alkyl spacer positioned between the molecular core and the active azobenzene chromophores. Species comprising spacers of sufficient length, and that exhibit a latent liquid-crystalline phase, feature efficient formation of stable, ordered domains in which the three side groups orient perpendicular to the polarization of the inscribing light beam. It is demonstrated that molecular order in these domains can be significantly improved by annealing at temperatures between the glass transition temperature and the clearing point of the specific compounds. This phenomenon allows combining the highly desirable processing characteristic of relatively short holographic writing times with small molecules in the fabrication of stable volume gratings, the latter feature so far having been reserved predominantly for polymeric species.

## Introduction

Azobenzene-based small organic compounds, that usually are designed to efficiently form surface relief gratings, are an emerging class of materials in the field of holographic applications[1] and as such could also be exploited for the purpose of optical data storage,[2–18] if it were not for the relatively poor stability in time of structures created with them. This phenomenon manifests itself in a decrease of the amplitude of refractive-index modulation $n_1$ – *i.e.* the difference in refractive index between irradiated ("inscribed") and unexposed ("non-inscribed") areas in such volume gratings. This is unfortunate, since small molecules can provide various advantages over macromolecular structures, amongst other things, ease of synthesis and purification and more freedom in molecular design. In addition, systems based on small molecules generally feature shorter writing times compared to their polymeric counterparts – clearly a technologically much sought-after advantage.[9] As a consequence, there remains a persistent need for small-molecular organic holographic materials that permit manufacture of volume gratings that are stable over time.

Promisingly, selected members of a recently introduced class of small-molecular trisazobenzene derivatives were found not to suffer from the above mentioned poor holographic stability.[19,20] As a matter of fact, refractive-index modulations created in films of some of those species did not only not decay with time, but, surprisingly, featured a rather remarkable "post-development", originating in an increase of $n_1$ after the writing laser was switched off that resulted in an *enhancement* of the contrast of the grating inscribed. This effect is known for certain macromolecular systems,[21–27] yet, for small organic molecules, this desirable phenomenon so far has been observed only for trisazobenzene compounds that featured mesophase(s) at elevated temperatures.[19,20] A detailed molecular structure–property relation that may explain this useful feature has, however, not yet been advanced.

In the present work, therefore, we focused on gaining a better insight into the origin of this attractive "post-development" of members of this trisazo family. For this purpose three compounds were selected which all contain photoactive side groups that are linked with amide moieties to a central benzene core in $C_3$-symmetry, with a spacer between the core and the azobenzene chromophore comprising methoxy substituents (see Table 1). The principal difference between the three species is the length of the decoupling spacer. As a consequence of the different molecular design, the phase behavior of the three derivatives varied: whilst compound **1** formed a molecular glass when cooled

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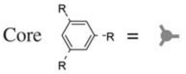
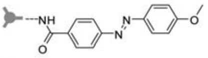
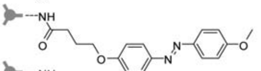
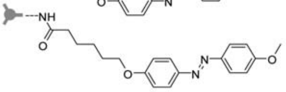
**Table 1** Chemical structures and phase characteristics of compounds explored[a,b]

| Compound | $T_g$ °C [a] | Transition temperatures °C [b] |
|---|---|---|
| Core  | | |
| *1*  | 134 | $\mathrm{G} \xrightarrow{187/233} \mathrm{Cr} \xrightarrow{305} \mathrm{Iso}$<br>$\mathrm{G} \xleftarrow{134} \mathrm{Iso}$ |
| **2**  | 64 | $\mathrm{Cr} \xrightarrow{232} \mathrm{Iso}$<br>$\mathrm{Cr} \xleftarrow{155} \mathrm{LC} \xleftarrow{167} \mathrm{Iso}$ |
| *3*  | 44 | $\mathrm{Cr} \xrightarrow{199} \mathrm{Iso}$<br>$\mathrm{Cr} \xleftarrow{114} \mathrm{LC} \xleftarrow{150} \mathrm{Iso}$ |

[a] $T_g$: glass transition temperature determined by differential scanning calorimetry (DSC) first-heating thermograms employing samples that were previously quenched from the melt in liquid nitrogen. [b] G: glass; Cr: crystalline; LC: liquid-crystalline; Iso: isotropic melt (all transitions correspond to peak temperatures of DSC second-heating/cooling thermograms).

from the isotropic melt, **2** and **3** featured liquid-crystalline (LC) phases at elevated temperatures, and were previously shown to display the favorable "post-development" of $n_1$.[20]

## Results and discussion

### Photo-induced alignment

In a first set of experiments, we attempted to elucidate the molecular origin of the photo-alignment of compounds **1**, **2** and **3** using polarized UV-vis and IR spectroscopy, as well as polarized optical microscopy. For this purpose, the three materials were spin-cast from solution into largely amorphous, thin-film structures, and subsequently illuminated at room temperature with polarized visible light for, respectively, 2 h for UV-vis spectroscopy and optical microscopy and 20 h for IR-spectroscopy studies.

After irradiation with polarized light ("writing"), films of the two derivatives **2** and **3**, featuring a latent LC phase, displayed a UV-vis absorbance that was strongly dependent on the direction of polarization of the incident "reading" light beam (Fig. 1, top), resulting in dichroic ratios, $D$, of, respectively, 1.9 and 2.6. Consistently, when illuminating thin-film architectures of, for instance, **2**, a pronounced, light-induced birefringence was observed in the irradiated areas (*cf.* Fig. 2, left). By strong contrast, only a faint optical anisotropy (dichroic ratio of maximum 1.3, Fig. 1) and significantly reduced birefringence were detected in the irradiated films of **1**.

Interestingly, for all three compounds, the strongest absorption, which is along the azobenzene chromophores (denoted here as 0°-orientation), was observed perpendicular to the polarization direction of the writing irradiation. In addition, in IR spectroscopy, in which we focused on the carbonyl groups (located at the core of the trisazobenzene derivatives) and the methoxy end-groups (Fig. 3, respectively, top and bottom), a strong anisotropy was found for the vibrations resulting from the latter moieties ($\nu_{\mathrm{OMe}}(\mathbf{1}) = 1255\ \mathrm{cm}^{-1}$, $\nu_{\mathrm{OMe}}(\mathbf{2}) = 1248\ \mathrm{cm}^{-1}$, $\nu_{\mathrm{OMe}}(\mathbf{3}) = 1249\ \mathrm{cm}^{-1}$);[28–32] this was most pronounced for compound **3**. Vibrations associated with the carbonyl moieties ($\nu_{\mathrm{C=O}}(\mathbf{1}) = 1655\ \mathrm{cm}^{-1}$, $\nu_{\mathrm{C=O}}(\mathbf{2}) = 1669\ \mathrm{cm}^{-1}$, $\nu_{\mathrm{C=O}}(\mathbf{3}) = 1664\ \mathrm{cm}^{-1}$),[28–32] in strong contrast, were virtually not affected by exposure to linearly polarized visible light of thin films of all three trisazobenzenes.

Hence, it appears that the short flexible spacers in species **2** and **3** allow the side groups linking the optically active azobenzene moieties to move relatively independently of the central core. As a consequence, upon irradiation with polarized light, the molecules seem to arrange into a "fork-like" conformation of the side groups, as schematically depicted in Fig. 2, right, in agreement with both UV-vis and IR spectroscopy data. This would explain why these trisazobenzene compounds of latent LC nature display significantly enhanced photo-alignment effects in comparison with those that do not form this mesophase (*i.e.* compound **1**) – since such phase can be expected to facilitate the formation of ordered domains. In compound **1**, on the other hand, in which the side groups are directly linked to the amide bond at the central core, reorganization of the azobenzene moieties is restricted.

### Stability of photo-induced alignment

In order to scrutinize the long-term stability of the photo-alignment of the three trisazobenzene derivatives, the temporal evolution of the dichroic ratio of irradiated films of the compounds was recorded over a period of 60 days. The results are summarized in Fig. 1. For both derivatives **2** and **3**, the photo-induced dichroic ratio was not only highly stable in the time frame investigated, but, indeed, *increased* in the first 10 days after irradiation before reaching saturation. For instance, a change in $D$ from 2.6 to 3.2 was observed for photo-aligned films produced with compound **3**. This phenomenon was less pronounced for **2**, for which $D$ increased from 1.9 to 2.0. For compound **1**, which does not feature a liquid-crystalline phase, by contrast, the dichroic ratio $D$ actually *decreased* from 1.3 to 1.2, already during the first 24 h.

### Annealing

Annealing is often used to increase the molecular order in architectures of liquid-crystalline compounds. Therefore, the effect of heat treatment on the photo-alignment in the above trisazobenzene structures was explored in experiments, in which the dichroic ratio $D$ and the amplitude of the refractive-index modulation $n_1$ created at room temperature were probed *in situ* at different temperatures using variable-temperature UV-vis spectroscopy and holographic experiments, respectively (for details see Experimental).

Pronounced amplification of both $D$ and $n_1$ was observed for compounds **2** and **3**, when reading was carried out at elevated temperatures (Fig. 4). Reassuringly, a similar development of $D$ and $n_1$ with temperature was found in holographic experiments and UV-vis spectroscopy, with the maximum amplification observed for both LC compounds analyzed above their glass transition temperature, $T_g$ (*cf.* Fig. 4), where the dichroic ratio nearly doubled and $n_1$ increased by more than 40% for **3**. Only when heating the thin-film structures to even higher

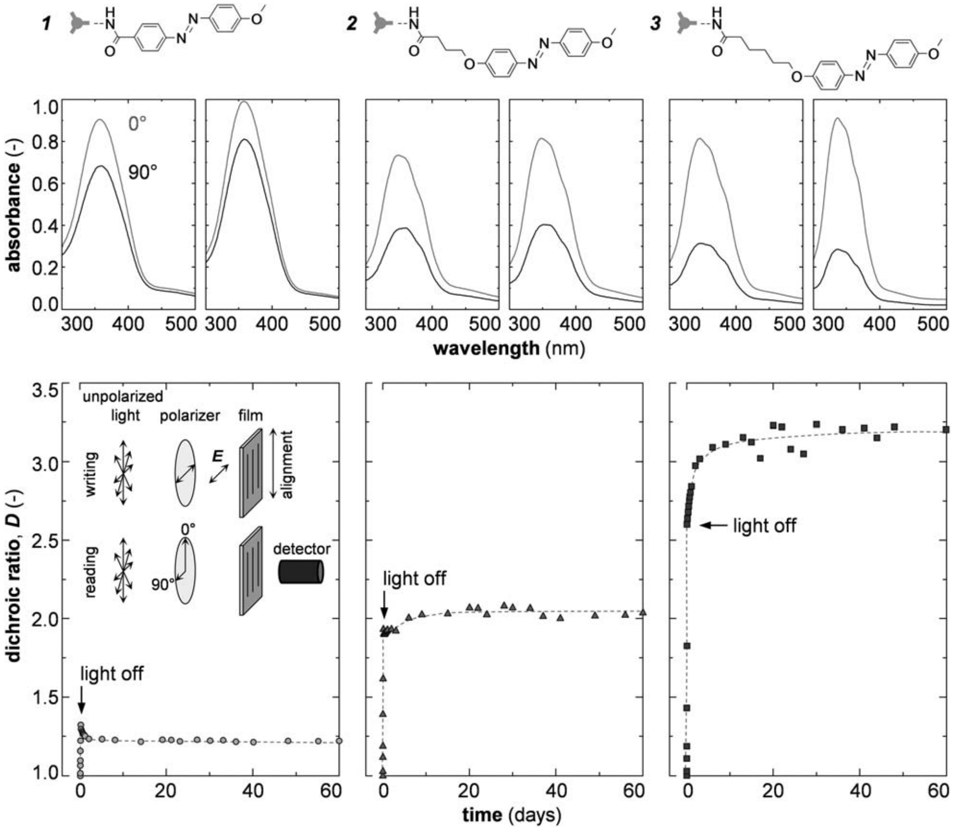


**Fig. 1** Photo-alignment at room temperature. Top: polarized UV-vis spectra of thin films of compounds **1**, **2** and **3** recorded with polarizers positioned at 0° and 90° angles (0°: parallel to the absorbing azobenzene chromophore/perpendicular to polarization of writing light) directly after 2 h exposure to linearly polarized light (left) and after 60 days storage in the dark (right). Bottom: corresponding temporal evolution of the dichroic ratio $D$ (ratio between absorbance at 90° and 0°) at $\lambda_{\max}$ of the unexposed films: $\lambda_{\max}(\mathbf{1}) = 356$ nm; $\lambda_{\max}(\mathbf{2}) = 347$ nm; $\lambda_{\max}(\mathbf{3}) = 345$ nm. Dashed lines are drawn as a guide to the eye only and the end of the writing process is indicated with arrows. Whereas a stable photo-induced alignment and an additional "post-development" are observed for LC derivatives **2** and **3**, a decrease in $D$ is found for the molecular glass **1**. Configurations used for writing and reading are schematically depicted in the inset.

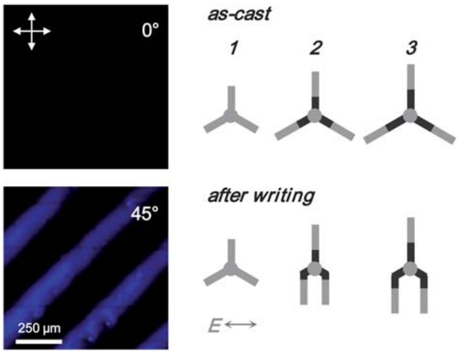


**Fig. 2** Left: polarized optical micrographs of a photo-induced pattern inscribed in a spin-coated thin film of compound **2**, taken at 0° and 45° with respect to the polarizer/analyzer system (indicated with white arrows). Right: simplified illustration of the alignment of the chromophores of the selected trisazobenzene derivatives upon exposure to linearly polarized light. Only in compounds **2** and **3** with decoupling spacers between the central core and the azobenzene units, the side groups were found to align perpendicular to the polarization direction of the writing light and allow formation of ordered domains. By contrast, in molecular non-LC glass **1**, in which the chromophores are directly connected to the core, independent movement of the side groups was hampered.

temperatures, closer to their LC-to-isotropic transition, the optical anisotropy was lost, as indicated by a continuous decrease of $D$ to 1, and a concomitant reduction of the birefringence was observed in polarized optical microscopy. (NB: due to limits of the experimental set-up the holographic experiments were confined to temperatures <125 °C.) By contrast, the optical patterns created in the molecular glass **1** were already severely affected at $T \ll T_g$, as manifested by a rapid, continuous decrease of both $D$ and $n_1$.

Clearly, this thermally enhanced amplification of $D$ and $n_1$ may provide the interesting tool to increase the photo-induced optical anisotropy of holographic structures – without compromising their temporal stability – by applying suitable annealing procedures. To explore this further, thin films of **2** and **3** were irradiated for 2 h with polarized light at ambient conditions, followed by a 20 min annealing step at temperatures of 10 to 20 °C above $T_g$, *i.e.* at temperatures at which reading resulted in a maximum optical contrast (Fig. 4). This protocol resulted in a significant increase in $D$, measured at room temperature, compared to thin-film architectures that were illuminated for the same period of time, but without being subjected to such a heat treatment procedure (Fig. 5). As a matter of fact, for compound **3** an enhancement of the value of $D$ from 2.3 to 4.4 was found,

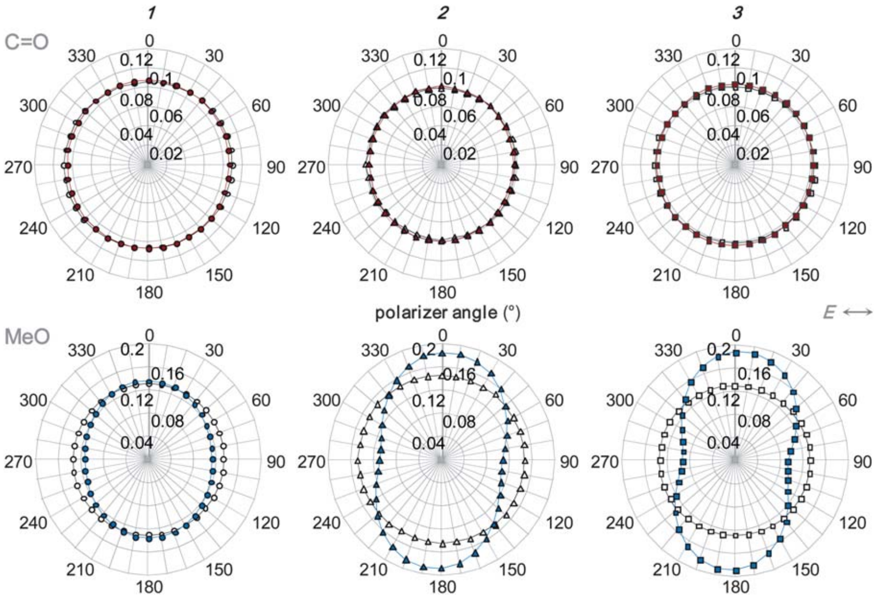


**Fig. 3** Polarized IR absorbance of the carbonyl (C═O; top) and the methoxy group (OMe; bottom) of compounds **1**, **2** and **3** (0°: parallel to the azobenzene moiety/perpendicular to polarization of the light used for the writing procedure): $\nu_{C=O}(\mathbf{1}) = 1655\ cm^{-1}$, $\nu_{C=O}(\mathbf{2}) = 1669\ cm^{-1}$, $\nu_{C=O}(\mathbf{3}) = 1664\ cm^{-1}$; $\nu_{OMe}(\mathbf{1}) = 1255\ cm^{-1}$, $\nu_{OMe}(\mathbf{2}) = 1248\ cm^{-1}$, $\nu_{OMe}(\mathbf{3}) = 1249\ cm^{-1}$. Spectra were recorded before (open symbols) and after (filled symbols) exposure to linearly polarized light. Whereas the carbonyl groups, located at the core of the molecule, remain virtually unaffected, the methoxy end-groups display a pronounced optical anisotropy in exposed films, *i.e.* an alignment perpendicular to the polarization of the inscribing light beam that increases with the spacer length. A derivation from perfect alignment, with a theoretical maximum of the absorbance at 0° polarizer angle, originates from experimental errors when calibrating and setting the polarizer manually.

which is an amplification that is more than three times the increase of the dichroic ratio over time (*i.e.* "post-development") observed for untreated films of this specific compound at room temperature (*cf.* Fig. 1).

### Photo-alignment at elevated temperatures

Finally, we also explored if exposure to elevated temperatures during the writing process provides additional means to manipulate the photo-alignment in trisazobenzene structures. Thereby we focused on compound **2**. Inscription – and for efficient data collection also subsequent reading – was conducted at isothermal conditions as a function of time (Fig. 6). Interestingly, writing times required to reach the maximum refractive-index modulations $n_1$ were found to decrease from ~10 s at ambient temperature down to ~1.5 s at ~85 °C, *i.e.* at $T > T_g$. However, this benefit was found to come at the expense of stability of the gratings at this temperature. From Fig. 6, for instance, it is clear that we were able to write stable gratings only at temperatures below the glass transition of this compound (~64 °C). Nonetheless, inscription of holographic gratings at elevated temperatures may still be exploited to reduce the writing times – provided writing is followed by subsequent rapid cooling of the active layers to room temperature.

## Conclusions

Small-molecular trisazobenzene derivatives with a latent liquid-crystalline phase were found to undergo a pronounced molecular realignment when exposed to linearly polarized visible light, while their non-LC counterpart was significantly less affected by the optical writing procedures. Polarized UV-vis and IR spectroscopies suggest that during writing, ordered domains form, in which the three side groups of these trisazobenzene compounds orient perpendicular to the polarization of the inscribing light beam, provided that a sufficiently long spacer is introduced between the molecule's core and the active chromophore moieties – as is the case in compounds **2** and **3**. Molecular order in these domains is improved relatively slowly at ambient conditions over a period of days (*cf.* Fig. 1), however, similar to more standard LC materials, this effect can be increased when following annealing protocols between $T_g$ and the clearing point (*cf.* Fig. 4 and 5). Apparently, during this amplification process, photo-induced ordered regions nucleate the less ordered surrounding, resulting in an enhanced overall alignment. However, if writing is conducted at too high temperatures, the high molecular mobility will not permit formation of such stable, oriented domains.

Clearly, the observed "post-development" of $n_1$ in the trisazobenzene derivatives **2** and **3** is interesting from a technological point-of-view, as it permits relatively short writing times, as well as fabrication of stable holographic intensity gratings. The contrast of these gratings can be adjusted not only with optical writing methods but also by exploiting suitable annealing procedures, offering an additional tool for designing them.

## Experimental

### Materials

The synthesis of the trisazobenzene compounds explored is described in ref. 20. Ultra-high molecular weight polystyrene

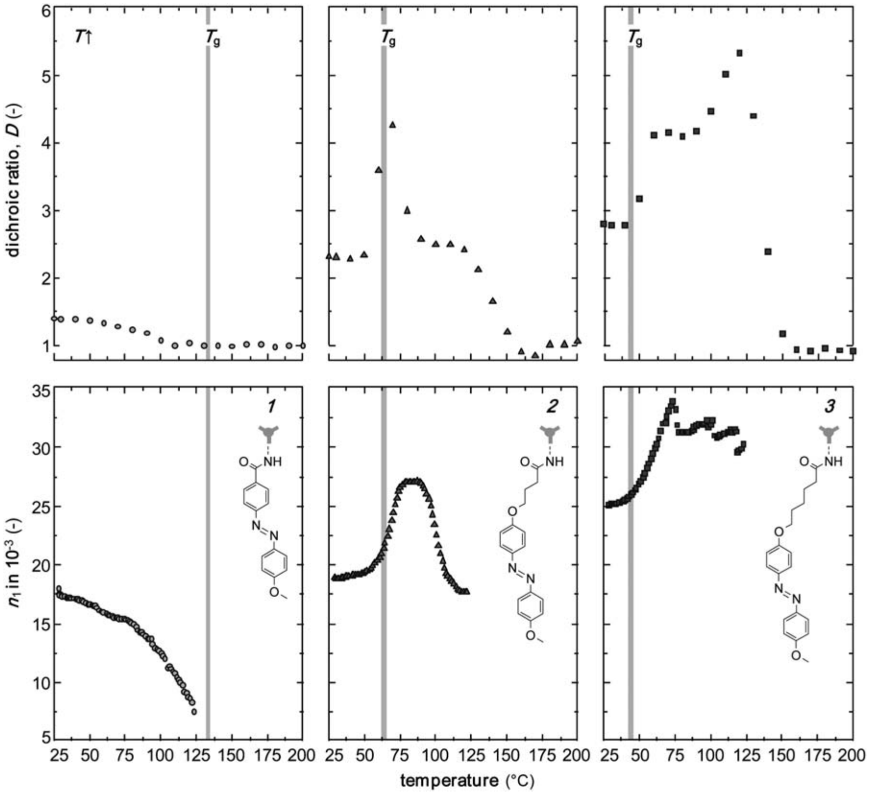


**Fig. 4** Development of the dichroic ratio $D$ (top) and refractive-index modulation $n_1$ (bottom) during heating of thin films of **1**, **2** and **3**, as deduced from variable-temperature polarized UV-vis spectroscopy and holographic experiments, respectively. Both datasets indicate a thermally induced amplification of the photo-induced alignment for LC structures **2** and **3** above $T_g$ (indicated with grey lines). Molecular order disappeared at temperatures close to the clearing point. In strong contrast, no amplification but a continuous decrease of the photo-orientation was found for compound **1** at temperatures already considerably below $T_g$.

(UHMW-PS) ($M_w$ ~30 000 kg mol$^{-1}$) was purchased from Poly sciences, Inc., Warrington, PA, USA.

## Thermal analysis

Differential scanning calorimetry (DSC) of the trisazobenzene derivatives was conducted under $N_2$ atmosphere at a scan rate of 10 °C min$^{-1}$ with a Mettler Toledo DSC 822e instrument. For this purpose, amounts of about 3 mg each compound were sealed in Al standard 40 µl crucibles. For determination of the glass transition temperatures ($T_g$), samples were heated to 260 °C or 310 °C in the case of **1** and subsequently quenched from the melt in liquid nitrogen.

## Thin-film preparation

Thin films of ~400 nm thickness for optical microscopy, spectroscopy and holographic characterization were prepared from 2 wt% tetrahydrofuran (THF) solutions (total content) that were heated to 55 °C for 60 min and subsequently cooled to room temperature. Resulting homogeneous solutions were spin-cast at ambient conditions with a Laurell WS-400B-6NPP/LITE spin-coater at 800 rpm onto glass slides. To increase the film thickness to a level required in holographic experiments, 5 wt% (respective to the solute) of ultra-high molecular weight polystyrene (UHMW-PS) was added to the solutions prior to heating.

## Photo-alignment

Photo-induced alignment of the azobenzene chromophores was performed at ambient conditions by exposure of thin films to linearly polarized light in a box of the dimensions 25 × 85 × 40 cm, fitted with an Osram® S Luminux® 9 W/860 (Daylight) source. The distance between sample and lamp was 10 cm in all experiments and a Polaroid HN-32 sheet polarizer was placed on top of the films. To inscribe patterns for optical microscopy studies, a shadow mask of 100 µm thickness was positioned between the sheet polarizer and the trisazobenzene films.

## Optical microscopy

Optical microscopy was carried out with a Leica DM4000 polarizing microscope.

## UV-vis spectroscopy

UV-vis spectra of thin films were recorded with a Perkin Elmer Lambda 900 spectrophotometer equipped with rotating Glan–Thompson polarizers. To characterize the development of dichroic ratios during the 2 h exposure phase and after certain storage periods in the dark, scans were taken from 280 to 700 nm at polarizer angles of 0°, 45° and 90° with respect to the alignment direction of the azobenzene chromophores. At the end of each measurement, a second spectrum was recorded at 0° to

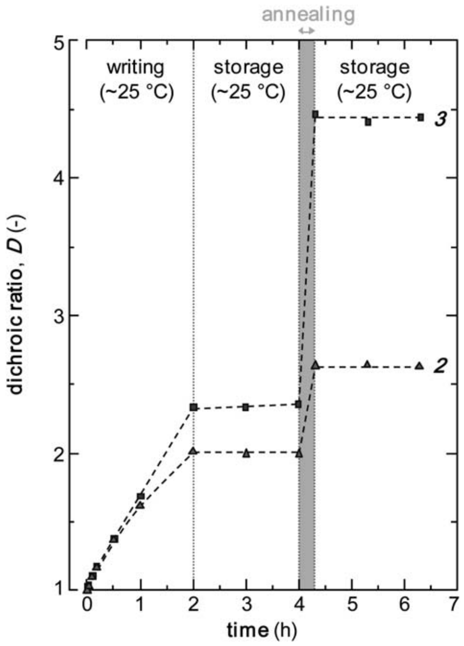


**Fig. 5** Temporal evolution of the dichroic ratio $D$ for compounds **2** and **3** during writing at ambient conditions and annealing at elevated temperatures of 10 to 20 °C above $T_g$ for 20 min. Before and after the annealing step the films were stored for 2 h at room temperature in the dark. The thermal treatment resulted in a remarkable increase of $D$ from 2.0 to 2.6 and from 2.3 to 4.4 for trisazobenzene derivatives **2** and **3**, respectively. Dashed lines are drawn as a guide to the eye only.

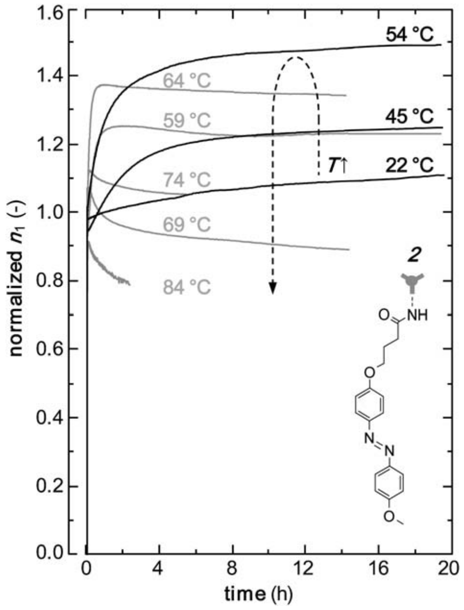


**Fig. 6** Amplitude of the refractive-index modulation $n_1$ as a function of time of thin films of compound **2**, normalized to unity when the writing laser was turned off. Inscription and reading of the holographic intensity gratings were conducted at isothermal conditions at different temperatures. Below $T_g$ (*i.e.* <64 °C), "post-development" was found to increase without sacrificing the stability. At higher temperatures, the stability decreased with increasing temperature, indicating that the formation of ordered domains is hampered.

ensure that no further undesired orientation effects were induced during the experiment. Variable-temperature UV-vis spectroscopy was performed under $N_2$ atmosphere employing a Harrick Scientific Products ATC-024-2 temperature controller equipped with a temperature-controlled demountable TFC-S25 flow cell. UV-vis spectra of each thin film were recorded at ambient conditions before and after 2 h exposure to linearly polarized light, as well as in steps of 10 °C over a temperature range from 30 to 200 °C.

### IR spectroscopy

IR spectra were recorded with a Bruker Vertex 70 spectrometer equipped with a Spectra-Tech IR polarizer. Scans were taken from 4000 to 600 $cm^{-1}$ before and after 20 h illumination with linearly polarized light, rotating the polarizer in 10° steps between 0° and 360°.

### Holographic experiments

The blue-green line (488 nm) of an argon ion laser was used to perform holographic experiments. A beam splitter generated two coherent parts of the laser beam, which were brought to interference in the sample plane. The diameter of the s-polarized laser beams was about 1 mm; the intensity of each beam was adjusted to 0.5 W $cm^{-2}$. The angle of incidence relative to the surface normal was ±14°, resulting in a grating period of about 1 μm. A laser diode at 685 nm, a wavelength range *outside* the absorption band of the azobenzene moiety, was used for *in situ* monitoring of the diffraction efficiency without affecting the writing process. To determine the diffraction efficiency, the power of the transmitted and the diffracted beam was measured with two photodiodes. For improving the signal-to-noise ratio, the laser diode was modulated and lock-in detection was used. Variable temperature holographic experiments were performed with a similar holographic set-up, but in this case the sample was placed in a temperature-controlled box. The equipment allowed adjusting the temperature in a range between 20 and 125 °C with an accuracy of 1 °C. To avoid a possible influence of effects related to the thermal history of the samples, a new film was employed for each experiment. The heating rate for reading at elevated temperatures was 0.4 °C $min^{-1}$.

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