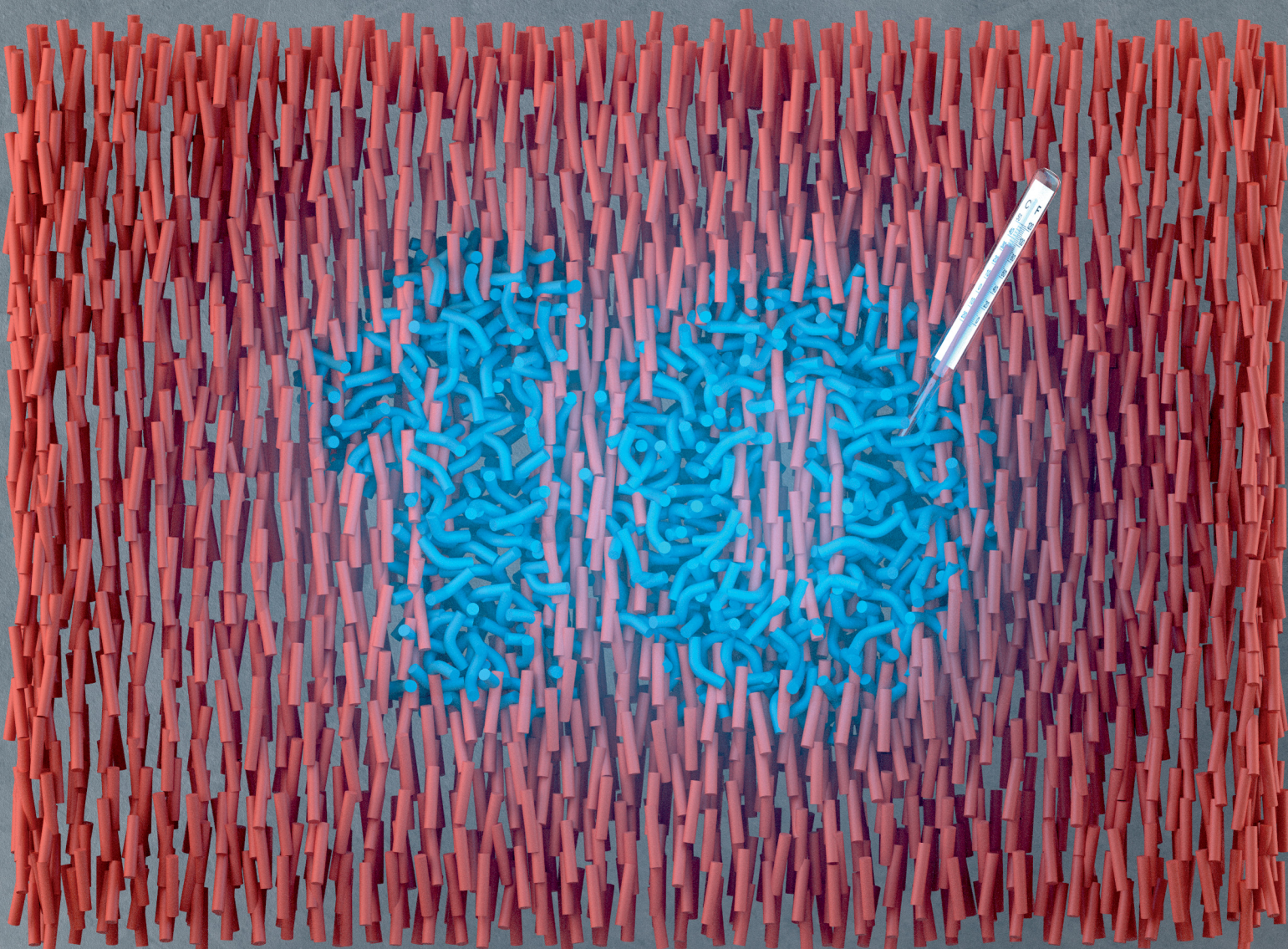


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**PAPER**

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## Light-induced bi-directional switching of thermal conductivity in azobenzene-doped liquid crystal mesophases†

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The development of systems that can be switched between states with different thermal conductivities is one of the current challenges in materials science. Despite their enormous diversity and chemical richness, molecular materials have been only scarcely explored in this regard. Here, we report a reversible, light-triggered thermal conductivity switching of  $\approx 30\text{--}40\%$  in mesophases of pure 4,4'-dialkyloxy-3-methylazobenzene. By doping a liquid crystal matrix with the azobenzene molecules, reversible and bidirectional switching of the thermal conductivity can be achieved by UV/Vis-light irradiation. Given the enormous variety of photoactive molecules and chemically compatible liquid crystal mesophases, this approach opens unforeseen possibilities for developing effective thermal switches based on molecular materials.

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## Introduction

Controlling the thermal conductivity of a material using an external stimulus could change the way we deal with the problem of thermal dissipation in microelectronics or the efforts to increase the efficiency of thermoelectric energy conversion devices. During the last few years, this research focused mostly on solid-state devices, particularly ferroelectrics: ferroelectric/ferroelastic domain walls are effective phonon scatterers, whose density can be regulated by an electric field and/or strain.<sup>1–3</sup>

In a soft-matter side approach to the problem, Ishibe *et al.*<sup>4</sup> showed that block copolymers may be engineered to show a reversible change in their thermal conductivity, although in this case is linked to the transition temperature between different types of ordering. Tomko *et al.*<sup>5</sup> achieved a large and

reversible switching of the thermal conductivity of bio-polymer networks upon hydration/dehydration cycles.

On the other hand, Shin *et al.*<sup>6</sup> use UV/Vis irradiation cycles to tune the thermal conductivity of photoresponsive polymers. Light modulates the  $\pi\text{--}\pi$  interactions among the polymer aromatic rings and triggers an actual crystal-to-liquid transition, resulting in a  $\sim 60\%$  change in the thermal conductivity.<sup>7</sup> This is a very controllable approach, which allows remote control of the thermal conductivity of the system, and whose only drawback is, perhaps, the lack of full reversibility of the liquid crystal (LC)-to-isotropic liquid (IL) in some photo-responsive polymers, which is sometimes compromised due to the lack of orientational mobility of the *trans* isomers at room temperature.<sup>8</sup>

This could be overcome by synthesizing azobenzene derivatives that self-assemble into 3D crystals or liquid crystals (LC) mesophases at or close to room temperature;<sup>9</sup> these form photo-active mesophases whose thermal transport could be directly modified by UV/Vis irradiation.

Here we report large (up to 40%) reversible switching of the thermal conductivity of photochromic 4,4'-dialkyloxy-3-methylazobenzene derivatives by isothermal UV/Vis illumination at room temperature.

More important, we demonstrate that photoactive 4,4'-dialkyloxy-3-methylazobenzene molecules can be doped into achiral LC matrixes to induce a complete and reversible molecular reorganization of the mesophase under UV/Vis irradiation and therefore a large change in the thermal conductivity of the whole system. Depending on the molecular arrangement of the host mesophase,

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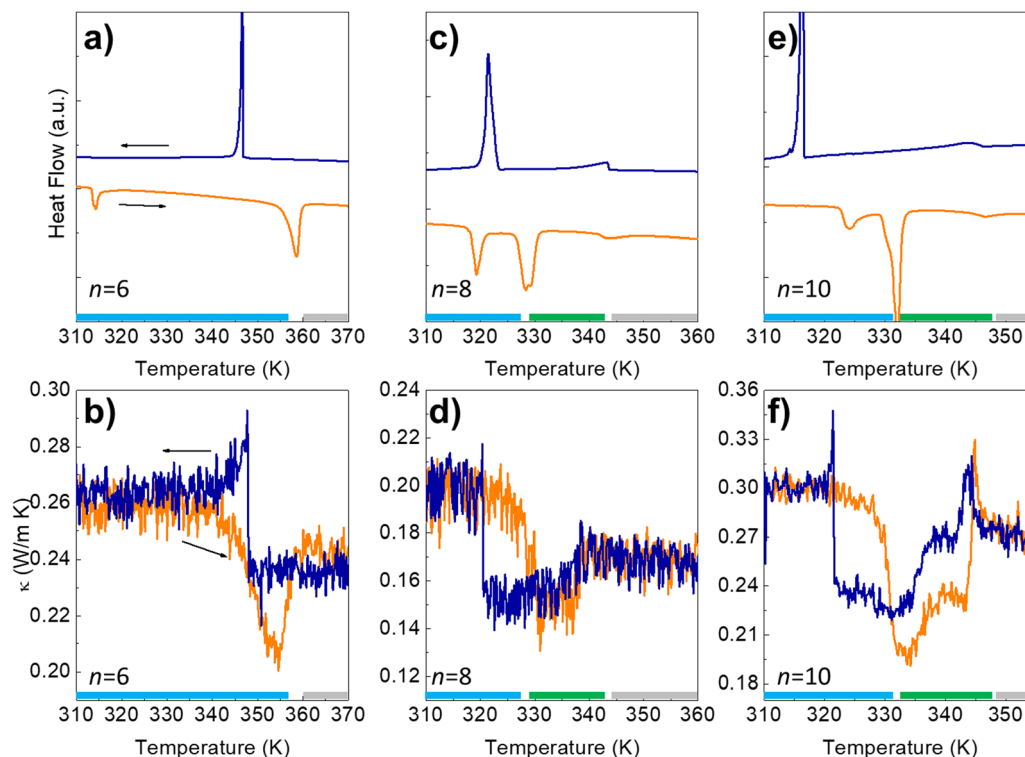
† Electronic supplementary information (ESI) available: Details of the synthesis, UV-Vis absorption spectra of the azobenzene films, DSC and POM scans, and NMR spectra of all the molecules synthesized for this work. See DOI: <https://doi.org/10.1039/d3tc00099k>

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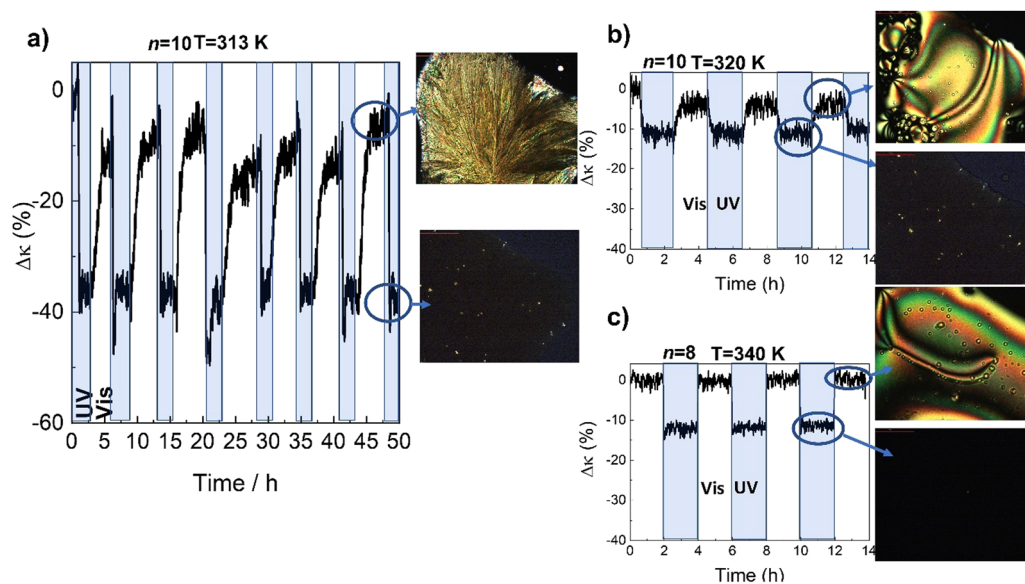






**Fig. 2** (a, c and e) Differential Scanning Calorimetry (DSC) and thermal conductivity (b, d and f) for the 4,4'-dialkoxy-3-methylazobenzene with  $n = 6$ , 8, and 10 carbon atoms in the alkyl chains. The sharp peaks at the lower temperature on the DSC heating runs correspond to a transition between two different 3D crystal structures, while the second one marks the transition between a 3D crystal and IL ( $n = 6$ ) or between a 3D crystal and a N-LC ( $n = 8$  and 10).<sup>11</sup> The broader peak at  $\approx 343\text{--}347\text{ K}$  in  $n = 8, 10$  marks the stability limit of this mesophase before melting into an IL. These transitions are perfectly visible in the thermal conductivity experiments (b, d and f). The temperature range of stability of the different phases is indicated by the color bars at the bottom of each panel (blue, green, and grey for the 3D crystal, N-LC and IL, respectively); see also the phase diagram of Fig. 1b).

transforms the crystal into *cis*-IL (see also Fig. S1, ESI<sup>†</sup>), with a reduction of the  $\kappa$  of  $\approx 30\text{--}40\%$ . Once UV irradiation stops, this phase change remains stable for hours in the dark, before recovering to the original phase after thermal relaxation of the



**Fig. 3** (a) Relative variation of  $\kappa$  in  $n = 10$  at 313 K under UV/Vis illumination. The transition corresponds to the isothermal 3D crystal-to-IL transformation, as shown in the POM images on the right. Relative variation of  $\kappa$  in  $n = 10$  at 320 K (b), and  $n = 8$  at 340 K (c), under UV/Vis illumination. At these temperatures, light drives the transition between the N-LC and the IL, as shown in the POM images at the right. Note the smaller thermal contrast compared to the 3D crystal to IL shown in panel (a).



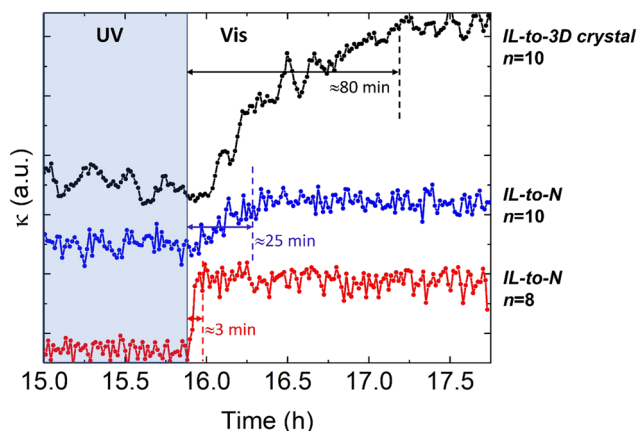


Fig. 4 Time-dependence of thermal conductivity during recovery of the ordered *trans*-phase, with visible light illumination of the isotropic-liquid in the *cis*-configuration. The figure shows the traces for the IL-to-3D crystal in  $n = 10$ , and the IL-to-N in the  $n = 10$  and  $n = 8$  (the same samples shown in Fig. 3). The curves have been displaced vertically for clarity. The recovery of the thermal conductivity is completed in 3 min for the IL-to-N of  $n = 8$ . The temperature of each experiment, as in Fig. 3, is 313 K (IL-to-3D crystal,  $n = 10$ ), 320 K (IL-to-N,  $n = 10$ ) and 340 K (IL-to-N,  $n = 8$ ), respectively.

*cis* azobenzene isomer. The recovery of the thermal conductivity can be accelerated by irradiating the IL with visible light (445 nm,  $\approx 150 \text{ mW cm}^{-2}$ ). As shown in Fig. 3a), this process can be repeated many times, demonstrating its reversibility.

Note that the observed reduction of  $\approx 30\text{--}40\%$  upon illumination means that  $\kappa$  in the *cis*-IL ( $\approx 0.2 \text{ W m}^{-1} \text{ K}^{-1}$ ) is considerably smaller than in the *trans*-IL ( $\approx 0.27 \text{ W m}^{-1} \text{ K}^{-1}$ ). We have measured a decrease of  $\approx 2\%$  in the density of the *cis*-IL compared to *trans*-IL, which seems too small to account for such a large change in  $\kappa$  ( $\approx 15\text{--}20\%$ ). Thus, this observation suggests a much less effective intermolecular (most likely  $\pi\text{--}\pi$ ) interactions among the bent molecules in the liquid.<sup>7</sup>

On the other hand, apart from a large thermal contrast between two or more states, an ideal thermal switch must transform among them as fast as possible upon application

of an external stimulus. In this case, although the crystal-to-liquid transition occurs within few minutes, the full recovery of the original thermal conductivity takes more than an hour. This is due to the low mobility of the large molecules at room temperature, which must diffuse through the liquid and reorganize to form back the *trans* crystal. This process is even more difficult in the case of molecules with longer alkyl chains. The recovery of the higher  $\kappa$  phase can be accelerated by reducing the length of the alkyl chains, and above all, by cycling between the higher mobility *trans*-N-LC and the *cis*-IL (Fig. 3b and c).

The speed of the process is shown in more detail for the different phases in Fig. 4 (see also Fig. S10, ESI†).

Following these results, we hypothesized that the 4,4'-dialkoxy-3-methylazobenzenes could be used as molecular machines to control the spatial arrangement of an achiral LC matrix, and hence its thermal conductivity. Doping a LC network with light-sensitive molecules has been used previously by several groups to induce macroscopic displacements, through cooperative bending, and transitional, and rotary motions of the molecules of the LC,<sup>17–20</sup> but this approach has never been applied to control the thermal conductivity of a mesophase.

To probe the viability of this hypothesis, we first searched for a system with a large thermal contrast between the LC mesophase and the IL, which is also chemically and structurally compatible with the 4,4'-dialkoxy-3-methylazobenzenes synthesized in this work.

We identified 4-octyl-4'-cyanobiphenyl (8CB) as a suitable candidate for this study.<sup>21</sup> DSC analysis shows that 8CB presents a smectic mesophase (Sm-LC) at room temperature, which is transformed into N-LC at  $\approx 306 \text{ K}$ , and then to an IL at 314 K (see the ESI† for a complete characterization of the pure 8CB and 8CB:azobenzene mixture; Fig. S13–S18, ESI†).<sup>22</sup> Our thermal conductivity experiments confirmed a reduction of  $\approx 15\text{--}20\%$  between the Sm-LC and IL phases; the N-LC phase of 8CB also shows a lower thermal conductivity than its IL (Fig. S14, ESI†). These results are in very good agreement with Marinelli *et al.*<sup>15</sup>, and confirm the planar orientation of the

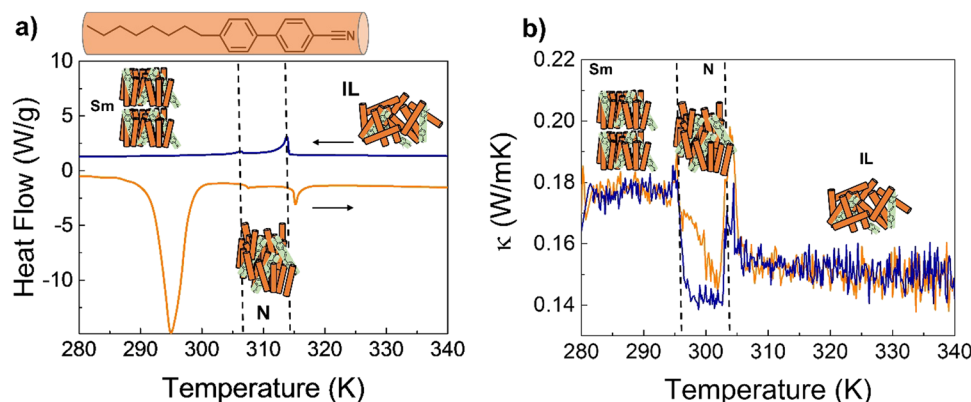


Fig. 5 (a) DSC heating and cooling scans of 8CB:azobenzene dispersion, identifying the thermal stability of the smectic, and nematic phases. (b) Temperature dependence (heating and cooling runs) of the thermal conductivity of 8CB:azobenzene, demonstrating the thermal contrast between the different phases observed in the DSC scan. The differences in the actual temperature of the transition temperatures measured by DSC and thermal conductivity are due to the different scan rates ( $10 \text{ K min}^{-1}$  in DSC and  $1 \text{ K min}^{-1}$  in thermal conductivity).







These photochromic molecules may act as light-driven molecular machines which reversibly operate over the bulk order of conventional LC mesophases, allowing reversible access to more than two thermal states and bi-directional switching of their thermal conductivity. Larger thermal contrasts may be observed in homeotropically aligned LC.

The variety of available LC, with different mesophases which could be accessed through doping with chemically compatible photoactive molecules, might open a new area of research for the design of molecular materials with multiple, accessible, thermal states around room temperature.

## Methods

4,4'-Dialkoxo-3-methylazobenzene derivatives were synthesized following a modification of a previously described route<sup>11</sup> (see the ESI† for a detailed description of the synthetic procedure). 4-Octyl-4'-cyanobiphenyl (8CB), was purchased from Sigma-Aldrich and used without further purification.

Structural characterization of these compounds was performed by <sup>1</sup>H-NMR using Bruker Advance DRX-500 and Varian Mercury-300 spectrometers. The recorded spectra are in agreement with the literature data.<sup>11,12</sup>

Polarized optical microscopy (POM) images were taken using a Leica DM2700 M microscope, equipped with a Linkam stage and a LNP96-S liquid nitrogen pump that allow precise control of temperature. UV-Vis absorption spectra were recorded on a Jasco V-630 spectrophotometer, coupled with a Jasco ETC-717 temperature controller. DSC measurements were carried out using a TA Instruments Q200 calorimeter. Thermal conductivity measurements were performed in a liquid nitrogen cryostat using a 3 $\omega$  method, with a home-made setup as described in ref. 13. Further details of all the procedures are provided in the supporting information accompanying this paper.

## Data availability

All data, and materials used in the analyses are available, upon reasonable request.

## Conflicts of interest

There are no conflicts to declare.

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