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Real-Time Sensing of the Thermal Diffusivity for Dynamic Control of Anisotropic Heat Conduction of Liquid Crystals

M. Motosuke · Y. Nagasaka

Abstract Molecular orientational order can be used to characterize the anisotropic behavior in mechanical, optical, and thermophysical properties. The creation of appropriate molecular orientation has the potential for producing a novel material or thermal switching device, which can control anisotropic heat conduction. Liquid crystals, which are widely used in display elements, have anisotropy not only in their optical, but also in their thermophysical properties, under given molecular orientational alignment conditions; this material can be a variable device with anisotropic heat conduction by controlling the molecular alignment. In the present study, a real-time sensing system for thermal diffusivity using the forced Rayleigh scattering (FRS) method was developed to investigate the transient behavior in the thermal anisotropy of nematic liquid crystals. This technique can be used to measure the in-plane thermal diffusivity perpendicular to the transient thermal grating created by interfering pulsed laser beams, and the thermal anisotropy of the sample can be determined using this non-contact method. The present FRS system can provide continuous measurements of the thermal diffusivity with subsecond time resolution, allowing evaluation of the dynamic behavior of anisotropy in the thermal diffusivity even during a transient process. In this article, the anisotropy of the in-plane thermal diffusivity of 4-4′-pentyl-4-biphenylcarbonitrile (5CB) with molecular alignment induced by either a rubbed substrate or an electric field has been measured. Also, the time evolution of the anisotropic thermal diffusivity in real-time under a dynamically controlled external elec-

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M. Motosuke (✉)
Department of Mechanical Engineering, Tokyo University of Science, 1-14-6, Kudannkita,
Chiyoda-ku, Tokyo 102-0073, Japan
e-mail: mot@rs.kagu.tus.ac.jp

Y. Nagasaka
Department of System Design Engineering, Keio University, 3-14-1, Hiyoshi, Kohoku-ku,
Yokohama 223-8522, Japan

tric field has been measured. The experimental results demonstrate the capability of dynamic anisotropic control of heat conduction by molecular alignment variations.

Keywords Anisotropic heat conduction · Forced Rayleigh scattering method · Liquid crystals · Molecular alignment · Real-time measurement

1 Introduction

Recent rapid advances in micro- and nano-technology enable us to design and control certain aspects of the microscopic structure of materials such as intermolecular association, higher-order conformation, and orientational alignment of molecules. The flexible design of thermophysical properties by microstructural control is currently studied, and this could become a new trend of material design in the near future. Molecular orientation with certain regularity can create anisotropic transfer and collision characteristics of heat carriers [1], which result in anisotropy in thermal conductivity or thermal diffusivity. Materials with anisotropic heat conduction due to molecular alignment have already been developed for some advanced applications. For instance, a graphite sheet is highly oriented and has high anisotropy in heat conduction so that it can be potentially be applied as a novel heat control device for spacecrafts or electronic elements [2]. However, many studies about anisotropic thermal properties have focused only on the creation of static and permanent anisotropy of the material. Dynamic orientational control of molecules can lead to anisotropic variation of thermal conductivity or thermal diffusivity. Therefore, from the point of view of heat conductive control, alignment order control of molecules could potentially be applied in state-of-the-art thermal devices. In this sense, this type of thermal device can expend the range of thermal control, especially in scientific and industrial fields such as microscale technology.

Liquid crystals are well-known substances in which molecular orientation can be controlled by an external force. In the nematic phase, liquid crystalline molecules have no positional order like a liquid, but have orientational order like a solid crystal, so they are called a "meso-phase [3]." In a typical LCD (liquid crystal display), a thin layer of liquid crystals between two polarization plates acts as an optical transmittance switch by controlling the molecular alignment in the presence or absence of an electric field. Liquid crystals have anisotropic thermal conductivities and thermal diffusivities corresponding to the molecular alignment order as well as anisotropic optical properties. Therefore, it is possible to dynamically control the thermal conductivity or thermal diffusivity by varying the orientational alignment of molecules just as in the case of the optical switch. Fast anisotropic variations in heat conduction can be expected because the orientational response time of a typical nematic liquid crystalline molecule is of the order of milliseconds [4,5]. Therefore, it can be assumed that liquid crystals are good candidates to confirm the potential for novel control devices of anisotropic heat conduction.

In order to validate the possibility of anisotropic thermal control utilizing the alignment order of molecules, quantitative thermal property data related to the orientational transition, including the dynamic behavior, are essential. There have been various high-speed measurement methods developed for thermal properties [6,7]. However, they are not suitable for application to a transition process because of their very slow repetition rate. It is difficult to evaluate the dynamic characteristics of anisotropic heat conduction in real-time. The forced Rayleigh scattering (FRS) method is an optical measurement technique for determining the in-plane thermal diffusivity; this method has the potential for evaluation of the dynamic change in heat conduction due to molecular alignment. In the present study, we have applied our sensing system for the thermal diffusivity based on the FRS method for measurement of the dynamically changing anisotropic behavior of liquid crystals. The FRS system can perform non-contact measurements of the in-plane thermal diffusivity in real-time; the repetition rate can be set to 100 data/s [8]. The anisotropic behavior in the heat conduction of nematic liquid crystals under alignment conditions, in both static and dynamic states, was measured. This study aims to demonstrate the possibility of dynamic control of anisotropy in thermophysical properties by molecular operations.

2 Measurement Method

As mentioned above, the measurement technique used in the present study is the FRS method. The principle of this method is based on photothermal related phenomena, a transient thermal grating, and diffraction [9,10]. The sample in the cell is heated by an interference pattern of two pulsed laser beams of equal wavelength and intensity. The interference pattern induces a temperature and the corresponding refractive index distributions. By using a probing laser beam, diffracted light can be obtained because the refractive index distribution acts as a transient optical grating. After laser heating, the excited temperature distribution decays by heat conduction. Based on diffraction theory [11], the intensity of the first-order diffracted beam is proportional to the square of the temperature variation. Therefore, the intensity of the first-order diffracted beam I_1 after laser heating can be expressed as a function of elapsed time t as

$$I_1 \propto \exp\left(-\frac{2t}{\tau}\right), \tag{1}$$

where τ is the relaxation time of heat conduction. Consequently, the in-plane thermal diffusivity a can be determined from an analysis of the temporal decay of the diffracted signal. The equation takes the form,

$$a = \frac{1}{\tau}\left(\frac{\Lambda}{2\pi}\right)^2, \tag{2}$$

where Λ is the grating period of the interference pattern, which is determined by the wavelength of the heating laser and the crossing angle of the beams.

The features of this method are as follows: (a) due to the non-contact scheme by two separate lasers with different wavelengths, a non-invasive measurement for a dynamic transition process is possible. (b) The thermal diffusivity perpendicular to the transient thermal grating can be measured. Thus, extraction of the in-plane property can provide a quantitative evaluation of the anisotropic thermal diffusivity. (c) This method requires a short measurement time of 1 ms or less. High-speed sensing can potentially avoid uncertainty factors from the variation of properties during a measurement time period [8]. (d) Real-time sensing with a subsecond repetition rate can be performed. These characteristics clearly indicate the possibility of real-time anisotropy sensing during a rapid transition process in molecular orientation.

3 Experimental System

A schematic view of the experimental real-time FRS system is shown in Fig. 1. For heating, a continuous-wave CO_2 laser with a wavelength of 10.6 µm was employed. This laser has an infrared wavelength and can produce a temperature rise in various materials [12]. Thus, there is no need to add the absorbing dye substance into the sample. The short pulse of the CO_2 laser beam by a mechanical chopper (MC) is divided into two beams of equal intensity by a beam splitter (BS). In this study, the crossing angle of two beams was selected in order to set the grating period of the interference pattern to be around 50 µm, and the pulse duration time of the heating beam was set to 100 µs. A He–Ne laser with a wavelength of 632.8 nm is utilized as a probe light. Since the liquid crystals have anisotropy in the refractive index, this could affect the direction of the detected signal for the case of off-vertical impingement. In order to minimize this effect, a depolarization plate which can convert the polarization of probe light from a linear beam into a random one is employed. The time-dependent diffracted light obtained from a sample is detected by a photomultiplier tube (PMT) through focusing lenses, apertures, and an interference filter. The signal from the PMT is sent to a computer via an eight-bit A/D converter. The measurement area for the thermal property can be adjusted by the lens (L3); in this study, the region was selected at approximately 500 µm in diameter. A part of the heating pulsed beam is sampled by a partial reflection mirror (PM) and is monitored by using the LN_2-cooled HgCdTe detector (MCT) for a trigger for data acquisition.

The time resolution of real-time measurements of the thermal diffusivity can be determined by the instrumentation limit or the decay of the temperature rise in the sample. This experimental setup can achieve a highly effective sequence in successive data acquisitions so that it can perform the thermal diffusivity measurement every 10 ms. Otherwise, the thermal limit is mainly due to the decay of the temperature rise in the sample which corresponds to the intensity profile of the heating beams; the relaxation is used to determine the thermophysical and optical properties of the sample and physical parameters of the heating laser. An appropriate repetition rate for the proper real-time measurement needs to be selected.

The sample cell is shown in Fig. 2, which is fabricated from aluminum with optical windows and a spacer. The liquid-crystal sample is placed between two window plates separated by a spacer. An anti-reflection coated ZnSe window was employed at the front side, and a transparent glass substrate was used as the rear window. The spacer determines the sample thickness. In the present study, stainless steel (SUS304) foil and polyimide film with a thickness of 60 µm were used. The metal foil serves as an electrode, which induces an electric field into the liquid-crystal sample, and the polyimide

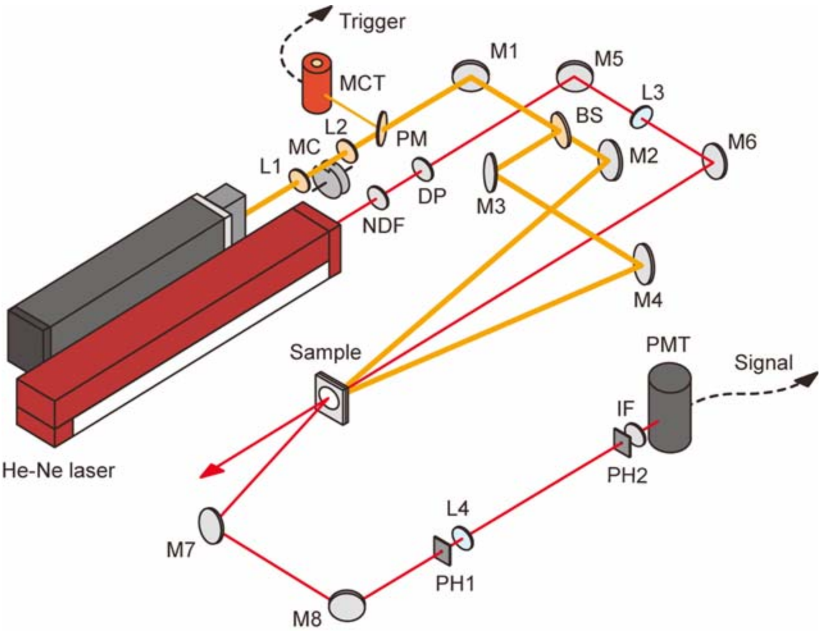

Fig. 1 Schematic image of the real-time measurement system by using the forced Rayleigh scattering method (FRSM)

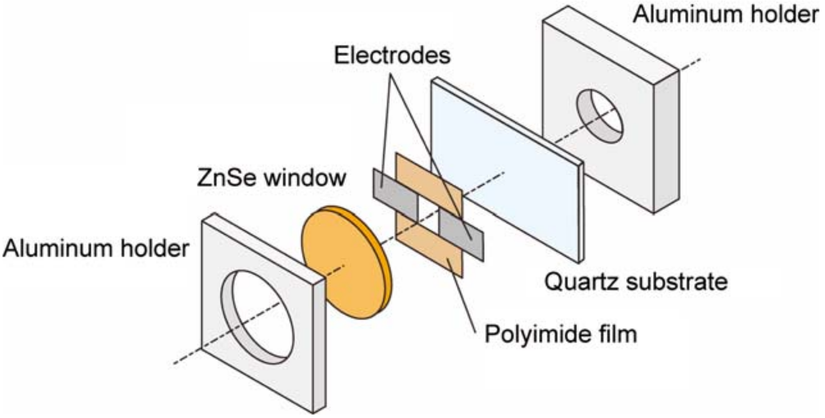

Fig. 2 Schematic view of sample cell. Electrode is made of stainless (SUS 304), and spacer is polyimide film. Measurement region is 500 μm in diameter and 60 μm in thickness. Sample volume is 60 μl

is an insulator. In this configuration, the electric field in the sample is parallel to the substrates. The electrode gap was set to 10 mm, and the applied voltage to the sample was controlled by a function generator and a high-voltage bipolar amplifier.

In this study, a 4-4′-pentyl-4-biphenylcarbonitrile (5CB) liquid crystal was used as the sample. The chemical formula of 5CB is illustrated in Fig. 3. 5CB has a mesogenic structure so that it is anisotropic in properties, such as the dielectric constant

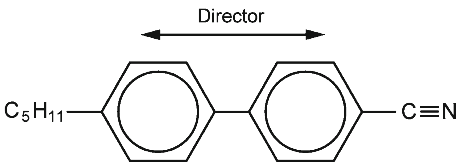

Fig. 3 Molecular structure of 4-4′-penthyl-4-biphenylcarbonitrile (5CB). Director of 5CB is parallel to the direction of long molecular axis

[13], magnetic susceptibility [14], and refractive index [15] in the smectic and nematic phases. In the present study, all experiments were conducted at room temperature (298 K); the sample in this report is assumed to be the nematic liquid crystal even with the temperature rise from laser heating for thermal diffusivity measurements. The director of the molecule which characterizes the orientational order is the direction parallel to the long molecular axis.

4 Results and Discussion

4.1 Measurement of Static Anisotropy in Thermal Diffusivity

As a preliminary experiment, thermal diffusivity measurements in the presence or absence of rubbing alignment were carried out. The thermal diffusivity of 5CB was measured by using a glass substrate without any treatment at angle increments of 30°. In this case, there is no orientational alignment in 5CB molecules. As a result, the difference in measured values of the in-plane thermal diffusivity at each angle was within 4%; there was no angle dependence in heat conduction. It means that the heat conduction of the sample is isotropic resulting from the random orientational order of the liquid crystal molecules.

Then we have used a rubbing-treated glass substrate for the rear window of the sample cell and measured the in-plane thermal diffusivity. In this case, it is possible for 5CB molecules to be aligned due to an anchoring force from the glass wall. Figure 4 shows detected signals for two angles; one is parallel to the rubbing direction, and the other is perpendicular to it. The relaxation processes of the two signals were obviously different; this fact illustrates that the heat conduction phenomenon in the rubbed direction is faster than that perpendicular to it. From this anisotropic behavior, it was found that the liquid crystal molecules oriented in the direction parallel to the rubbing treatment. The anisotropic ratio of the in-plane thermal diffusivity $a_{||}/a_{\perp}$ was estimated to be 1.45. The thermal anisotropy obtained from this experiment was rather low as compared with other reported ratios for 5CB [16]. This discrepancy is due to the differences of experimental conditions, especially in the anchoring force from the wall substrate to the liquid crystals. In our experiments, treatment to the substrate was only on one side, i.e., to the glass as the rear window. The induced orientational alignment in the sample was not so strong in such conditions. Through preliminary measurements, we can confirm that our experimental system can detect the anisotropic behavior in the in-plane thermal diffusivity of 5CB without any additive.

Additionally, we have measured the in-plane thermal diffusivity of electrically aligned 5CB molecules. Figure 5 shows the anisotropic thermal diffusivity data in

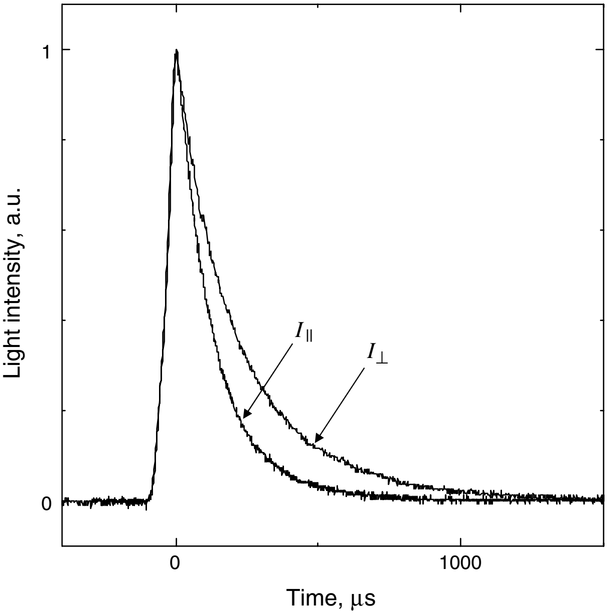

Fig. 4 Detected FRS signals by measurement with rubbing treatment quartz substrate. Diffracted light parallel to the rubbing direction $I_{||}$, and perpendicular to it $I_{\perp}$. Anisotropic ratio $a_{||}/a_{\perp}$ obtained from these signals was 1.45

the presence of an external electric field. The electric field intensity was $50\,\mathrm{V} \cdot \mathrm{mm}^{-1}$, and there was no special alignment or coating treatment, unlike the wall conditions of other studies [17]. In this experiment, the driving force to induce alignment of the sample was only the electric field. Since the direction of the electric field is parallel to the substrates, the director of the 5CB samples is parallel with the electric field, and the orientation of molecules is the so-called homogeneous alignment. The thermal diffusivity parallel to the electric field $a_{||}$ was larger than that normal to the field $a_{\perp}$. The anisotropic ratio was determined to be 1.92, higher than that of measurement results from the rubbing alignment. This value of the anisotropic ratio is similar to the reported ratios of other researchers using either rubbing or magnetic alignments. In addition, we also checked the creation of the molecular alignment in the sample through observation of the characteristic texture under the electric field by a microscope using polarized light.

Next, we discuss the relationship between the degree of molecular orientation and the anisotropy in the thermal diffusivity. A theoretical model describing the heat conduction of aligned liquid crystals [18] was used in the present study. According to this model, equations which can relate molecular alignment to the anisotropy in the thermal diffusivity are expressed as

$$a_{||} = \frac{a^*_{||}(1 + 2S) + 2a^*_{\perp}(2 + S)}{3}, \tag{3}$$

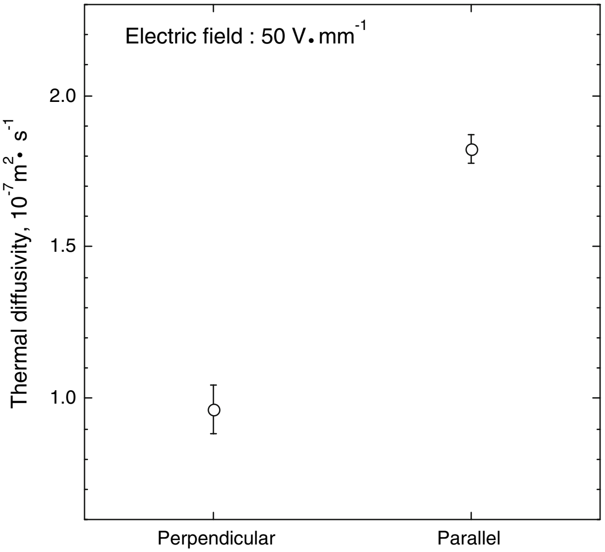

Fig. 5 Thermal diffusivity of 5CB with electric alignment. In these results, the anisotropic ratio $a_{||}/a_{\perp}$ is 1.92

$$a_{\perp} = \frac{a_{||}^{*}(1-S) + a_{\perp}^{*}(2+S)}{3}, \tag{4}$$

where S is the order parameter defined as follows;

$$S \equiv \frac{1}{2}\left\langle 3\cos^2\theta - 1\right\rangle, \tag{5}$$

where θ is the angle between the director and the long axis of each molecule, and the brackets denote an average over all molecules in the system. For perfect alignment, the order parameter is equal to one, and is zero for an isotropic or random condition. $a_{||}^{*}$ and $a_{\perp}^{*}$ are the normalized thermal diffusivities for the case of perfect alignment ($S = 1$). In this study, we use the following transformed equation:

$$S = \frac{a_{||}/a_{\perp} - 1}{a_{||}^{*}/a_{\perp}^{*} - 1}. \tag{6}$$

By using Eq. 6, it is possible to evaluate the macroscopic order parameter from the experimentally obtained thermal anisotropic ratio. The order parameter of the experimental results by using the rubbing treatment glass was estimated to be 0.35, and that for the case of the applied electric field was 0.72. The normalized anisotropic ratio $a_{||}^{*}/a_{\perp}^{*}$ used in this calculation was 2.27, which is the theoretical value in Ref. [18]. From comparisons of the calculated order parameters with those obtained from other methods, it was found that the rubbing alignment in the present study could not induce sufficiently strong molecular orientation and that the electrical alignment condition could be used to generate sufficient orientation of 5CB molecules.

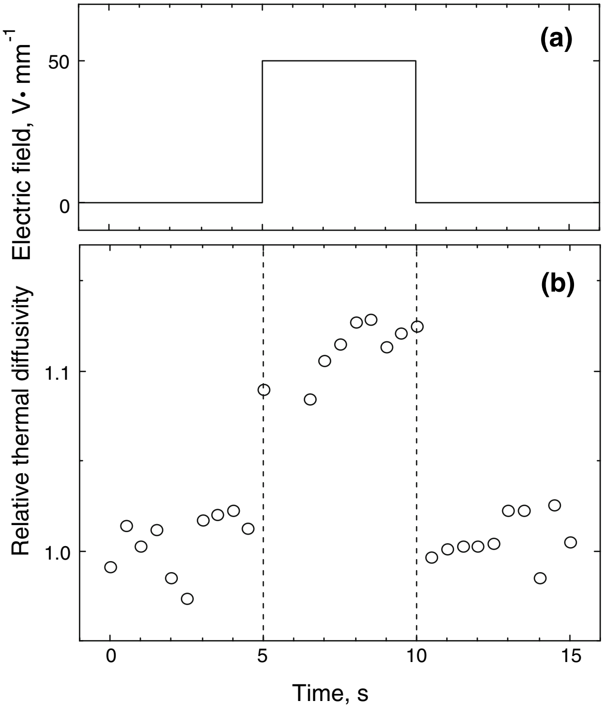

Fig. 6 Measurement results of time evolution in thermal diffusivity $a_{||}$ during voltage control: (**a**) variation of applied electric field and (**b**) normalized thermal diffusivity parallel to the electric field $a_{||}$

4.2 Real-time Control and Sensing of Anisotropic Thermal Behavior

Considering the applications for anisotropic devices in heat conduction, electrical alignment has an advantage in the flexible control of the external force to induce molecular orientation. In order to investigate the potential for dynamic control for anisotropic heat conduction by molecular alignment, we conducted real-time measurements of the in-plane thermal diffusivity in a transient process under a time-dependent applied electric field. The duration time of the applied voltage was 5 s. The time interval of the thermal diffusivity measurement was selected to be 500 ms considering the parameters of 5CB and experimental conditions. Figure 6 shows the time evolution of (a) the applied electric field and (b) the in-plane thermal diffusivity parallel to the electric field, $a_{||}$. The grating period was set to 51.9 μm. The measured value of the thermal diffusivity underwent a sudden increase as the voltage was applied, and then decreased as the electric field was turned off. The dynamic behavior of the thermal diffusivity corresponded to the applied electric field in liquid crystals. The sensitivity of both transient characteristics was in the subsecond range, which would imply the possibility of the use of a high-speed switch in anisotropic heat transfer by molecular alignment control. In this process, the induced thermal anisotropy in the sample was less than the results at static conditions of the electrical alignment. Although further investigations into the details of transient characteristics will be needed for quantitative discussion about the difference, we can confirm the potential for a variable thermal anisotropic device, which can control heat conduction by varying the molecular orientation. It is also indicated from our measurement results that the real-time FRS sensing system has the capability for evaluation of a transient process of anisotropic change in these conditions.

5 Summary and Conclusions

This manuscript reports the in-plane anisotropy in the thermal diffusivity of nematic 4-4′-pentyl-4-biphenylcarbonitrile (5CB) liquid crystals in both static and dynamic conditions of molecular alignment. Measurements were carried out by a real-time sensing system based on the forced Rayleigh scattering method using an infrared laser. The anisotropic behavior of the in-plane thermal diffusivity of 5CB under electrically induced homogeneous alignment was higher than that of the same sample under a rubbing alignment. The experimental system can detect the transient variation of the thermal diffusivity of the liquid crystals under an applied time-dependent electric field. The thermal diffusivity rapidly changed in response to the applied external field with subsecond sensitivity. This behavior clearly indicates the potential for dynamic control of anisotropic heat conduction by varying the molecular orientation. In addition, we can validate the capability of real-time sensing by using the forced Rayleigh scattering method for evaluation of the transient behavior in the anisotropic thermal diffusivity with a high repetition rate in the millisecond region.

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