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## Liquid Crystals

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## Preliminary communication

# First observation of an optically controlled electro-optic effect in nematic-discotic liquid crystals†

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An optically controlled electro-optic effect in nematic-discotic liquid crystals was discovered for the first time. The peculiarities of this effect are: (a) high photosensitivity observed in three different radial multiyne liquid crystal materials, allowing optically controlled transmission, i.e. giving the possibility of writing and reproducing optical images; (b) for one of these compounds (**1a**) the effect occurs at temperatures far below its melting point and even at room temperature.

The search for new materials and effects for writing, reading and the storage of optical information is currently of great interest. Liquid crystals are one of the promising materials for such optical devices. Electrically controlled liquid crystal displays have widespread applications. In optically controlled systems, liquid crystals are used only in sandwich arrangements with photoconductive layers as, for instance, in spatial light modulators using ZnS [2], Si [3],  $\alpha$ -Si [4] or other photoconductors. Recently, the possibility of movable, photoinduced charge carriers in calamitic and disc-like liquid crystals has also been shown [5, 6].

Due to their high modulation characteristics in combination with the photoconductivity observed in them, liquid crystals have indeed become strongly promising materials for optically addressed equipment. In this paper, we report and discuss preliminary results concerning the observation of an optically controlled change of transmission through a cell made of glass and filled with nematic-discotic liquid crystal material. The molecular structures of the materials used, the so-called *radial multiynes*; and their phase transition temperatures are shown in figure 1.

Because the N<sub>D</sub> phase of **1a** has the best ability to be

supercooled, and it is noteworthy that the phase is completely stable in a closed cell at ambient temperature for extremely long periods of time, most of our preliminary electro-optical trials discussed in this communication were focused on this particular pentayne. The two other members, **1b** and **2**, of our available series of radial multiynes shown in figure 1 are also suitable and exhibit similar electro-optic effects but, because of their high tendency to crystallization, only at elevated temperatures.

With regard to the relationship between the molecular structures of the three flat and highly unsaturated compounds **1a**, **1b**, and **2** and their electro-optical properties described here for the first time, it seems to us important to emphasize that *neither* the number of phenylethynyl units *nor* the type of functionalization of the alkoxy chain in **1a** or **1b** plays a significant role, neglecting of course their influence on the transition temperatures of these radial multiynes.

After the application of an electric field to a cell filled with **1a**, there begins a reorientation of the molecules and the appearance of colours which are connected with the change in birefringence. At a voltage of 6 V a domain structure appears (figure 2) which is very similar to the Kapustin–Williams domains observed in calamitic nematic phases [10]. This domain texture is preserved under increasing voltage, but the periodicity and the colours change. The formation of domains is connected with a

†This paper is part 112 of the Berlin research group on liquid crystalline compounds; for part 111 see [1].

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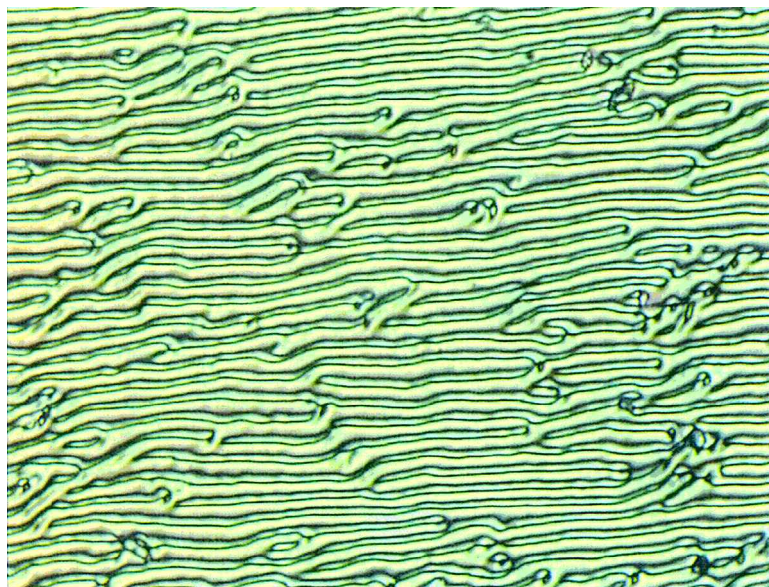


Figure 2. Domain structure of the  $N_D$  phase of pentakis[(4-pentylphenyl)ethynyl]phenyl 10-carbethoxydecyl ether (**1a**) at a voltage of 6 V.

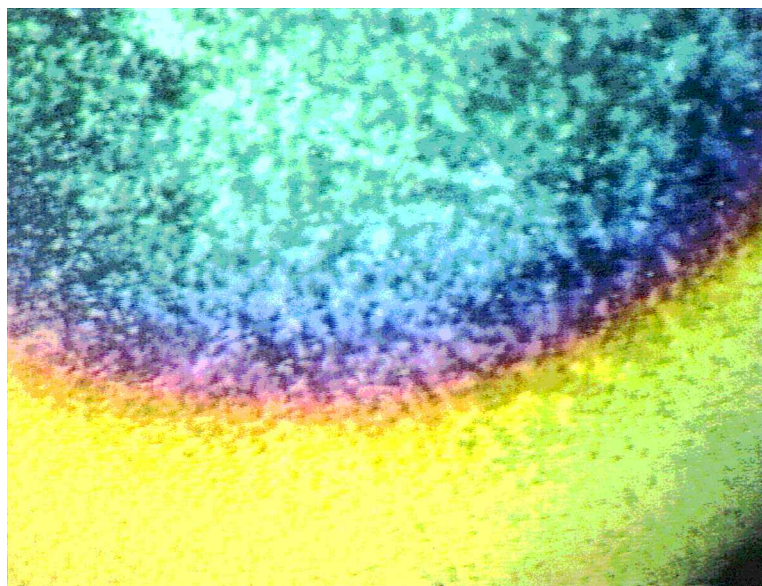
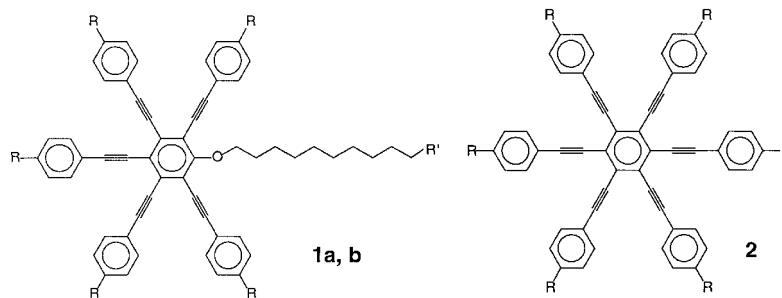


Figure 3. Snapshot of the texture obtained in a cell filled with the radial multiynyl alkyl ether **1a** as viewed microscopically using crossed polarizers, with application of an electric field (6 V) and after partial illumination with white light. This photograph illustrates the contrast between the illuminated area (blue–green with a violet edge) surrounded by the optically unaffected (green–yellow) region of the sample.

current flow in the cell. In high electric fields hydrodynamical processes could in fact be observed in the polarizing microscope. Illumination of the sample studied (diameter of this area: 1 mm; conventional white light source of the microscope) causes an interesting effect: the illumination leads to a change of colour. This colour change is local (figure 3) and is reversed after shutting off the light; this process can be repeated countless times,

and the cell used seems not to suffer. The size of the central part (blue–green in colour) of the microscopic picture corresponds with the diameter of the light beam. The red and yellow colours are the result of a diffusion of charge carriers across the border of the illuminated area. This diffusion causes a change in the potential distribution outside this part of the cell. In figure 4, the change of colours seen in the microscope using crossed



Radial Multiyne	R	R'	Cr → N <sub>D</sub>	N <sub>D</sub> → I
<b>1a</b> [7]	C <sub>5</sub> H <sub>11</sub>	COEt	56.6 / 57.9 (51.6)	69.0 / 69.2 (0.3)
<b>1b</b> [8]	C <sub>5</sub> H <sub>11</sub>	CH <sub>3</sub>	75.0 / 74.5 (34.0)	101.0 / 101.4 (0.2)
<b>2</b> [9]	C <sub>7</sub> H <sub>15</sub>	—	98.2 / 99.0 (44.4)	131.2 / 132.6 (0.4)

Figure 1. The molecular structures and phase transition data for the two pentakis[(4-pentylphenyl)ethynyl]phenyl 10-carbomethoxydecyl and undecyl ethers (**1a** and **1b**) [7,8] as well as for hexakis[(4-heptylphenyl)ethynyl]benzene (**2**) [9]. The temperatures in °C were determined by polarizing microscopy (PM) and by DSC on heating at 1°C min<sup>-1</sup>; the transition enthalpies (kJ mol<sup>-1</sup>) are given in brackets. The presentation of these data is as follows: PM/DSC ( $\Delta H$ ); Cr: crystalline, N<sub>D</sub>: nematic-discotic, I: isotropic liquid.

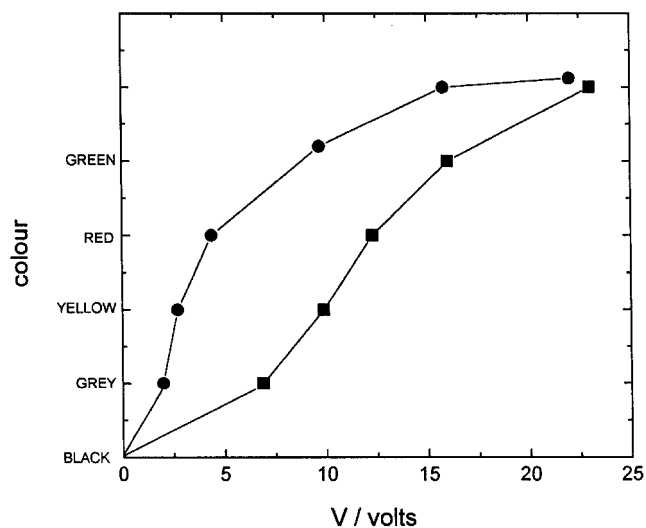


Figure 4. Colour changes of the N<sub>D</sub> texture of **1a** with change in applied voltages. Colours were those observed using crossed polarizers and either with illumination with white light (●) or without it (■). At the start of these measurements the sample appears black due to the homeotropic alignment of the nematic-discotic radial multiyne.

polarizers is shown as a function of the applied voltage for samples with or without illumination. In a d.c. electric field, the liquid crystal cell used here is more sensitive, with the illumination of the positive electrode leading to an enhancement of the negative charge, which is in accordance with other findings [5]. Currently, details are not known about the origin of this charge.

We feel it is important to emphasize the high stability of the radial multiynes studied here, e.g. cells filled more than one year ago still work without losing their characteristics in spite of the frequent action of electric fields and light. These findings could be of interest for optical data processing systems. For a complete interpretation, more detailed investigations are in progress including also trials with other types of disc-like mesogens.

The above studies were performed using a polarizing microscope equipped with a microscope CCD-camera and conventional sandwich cells (thickness 5–9 μm) made of glass plates coated with (transparent) tin oxide electrode material and a thin orientational layer to which d.c. or a.c. voltages could be applied. The preparation of the probe was carried out by heating each of the disc-like, flat N<sub>D</sub> mesogens into their isotropic liquid phases, filling the cell, and cooling it slowly down to room temperature (~25°C); the sample (**1a**) was then in the nematic-discotic phase—greenish yellow to the eye. Homeotropic alignment of the materials (**1a**, **1b**, or **2**) took place during the transition from the isotropic phase into the nematic-discotic phase. However, under an electric field, strong fluctuations could be seen in the polarizing microscope. On supercooling them below their melting points the preparations of **1b** and **2** crystallize, whereas that of **1a** stays stable in its mesophase at room temperature for a long period, i.e. more than 30 K below its melting point, without or in an applied electric field (up to 20 V).

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