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A new memory effect: smectic liquid crystalline memory having both conductive and optical memory

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We report a memory effect of a smectic liquid crystal that is conductive. The smectic liquid crystalline materials investigated have two long alkyl chains and a long conjugated core. On forming the smectic phase, molecules order to form a continuum of conjugated cores. Since the latter is conductive as a result of charge hopping, smectic molecular ordering of these compounds produces charge transport ability. Because of the strong dispersion force between the alkyl chains, after cooling the smectic molecular order is memorised at room temperature. In addition, the charge transport ability is also memorised (*1*). The conductivity of a device with smectic liquid crystalline order is about 5×10^7 times larger than that of a device that does not have any smectic order. Therefore, by using laser beam spot heating or by electrical heating, conductive spots can be written. These spots also can be read both by optical and electrical methods. Therefore, this is the first new type of memory that can be written and read both electrically and optically.

There are essentially three types of memories in our society: semiconductor memory, magnetic memory and phase transition memory. The first is used in D-RAM (dynamic random access memory), the second in a hard disc and the third in DVD discs.

The first memory can be written and read electrically, the second memory can be written and read magnetically, whereas the third memory can be written and read optically. However, there is no memory that can be written and read both electrically and optically.

In this paper, we report such a new type of memory: the conductive liquid crystalline memory that can be written and read by both electrical and optical methods and which uses new conductive thermotropic liquid crystalline materials. These smectic liquid crystalline materials have two long alkyl chains and a long conjugated core. By forming the smectic liquid crystalline phases, molecules order to form a continuum of long conjugated cores. Because the continuum of conjugated cores is conductive by charge hopping, smectic molecular ordering of these compounds produces charge transport ability. Because of the strong dispersion force between the long alkyl chains, after cooling the smectic molecular order is memorised at room temperature. Therefore, the charge transport ability is also memorised. Therefore, conductive spots can be written by electric heating or laser beam heating (see Figure 4) and then they are memorised. As these spots have both conductive ability and optical anisotropy, they can be read two different ways, electrically and optically. The chemical structures of the new conductive liquid crystalline materials are shown in Figure 1 and Table 1. These compounds

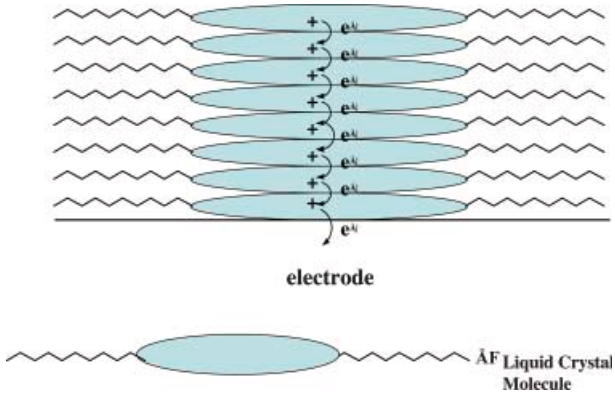
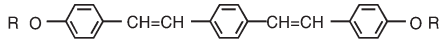


Figure 1. Charge transport in the smectic liquid crystal phase.

Table 1. Phase transition temperatures of the new liquid crystalline compounds.



R	Transition temperatures/°C
$C_{10}H_{21}$	Cr 98 SmG 187 SmF 250 SmC 255 N 270 I
$C_{11}H_{23}$	Cr 138 SmG 184 SmF 247 SmC 266 N 268 I
$C_{12}H_{25}$	Cr 137 SmG 179 SmF 242 SmC 300 N 313 I
$C_{15}H_{31}$	Cr 139 SmG 160 SmF 220 SmC 246 N 248 I

Cr=Crystal, SmG=crystal smectic G, SmF=smectic F, SmC=smectic C, N=nematic, I=isotropic.

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have a long conjugated core and they order in the smectic phase, which must be advantageous for transport of charge between the molecules.

In a liquid crystalline cell having ITO electrodes, these compounds exhibited a conductivity of 70–530 $\mu A\,cm^{-2}$ in the smectic liquid crystalline phase (applied voltage 5 V, cell gap 15 μm). The phase behaviour of these liquid crystalline materials has been measured. Measurement of transition temperatures and assignment of the mesophases were carried out by means of a micro melting point apparatus equipped with polarisers and a differential scanning calorimeter (DSC), and by X-ray diffraction. The compounds exhibit three phases, the crystal smectic G phase and the smectic F and C phases (*1*). In the X-ray diffraction pattern of this compound, the sharp peak in the small-angle region indicates that the layer spacing of this smectic phase is 39.3 Å; the

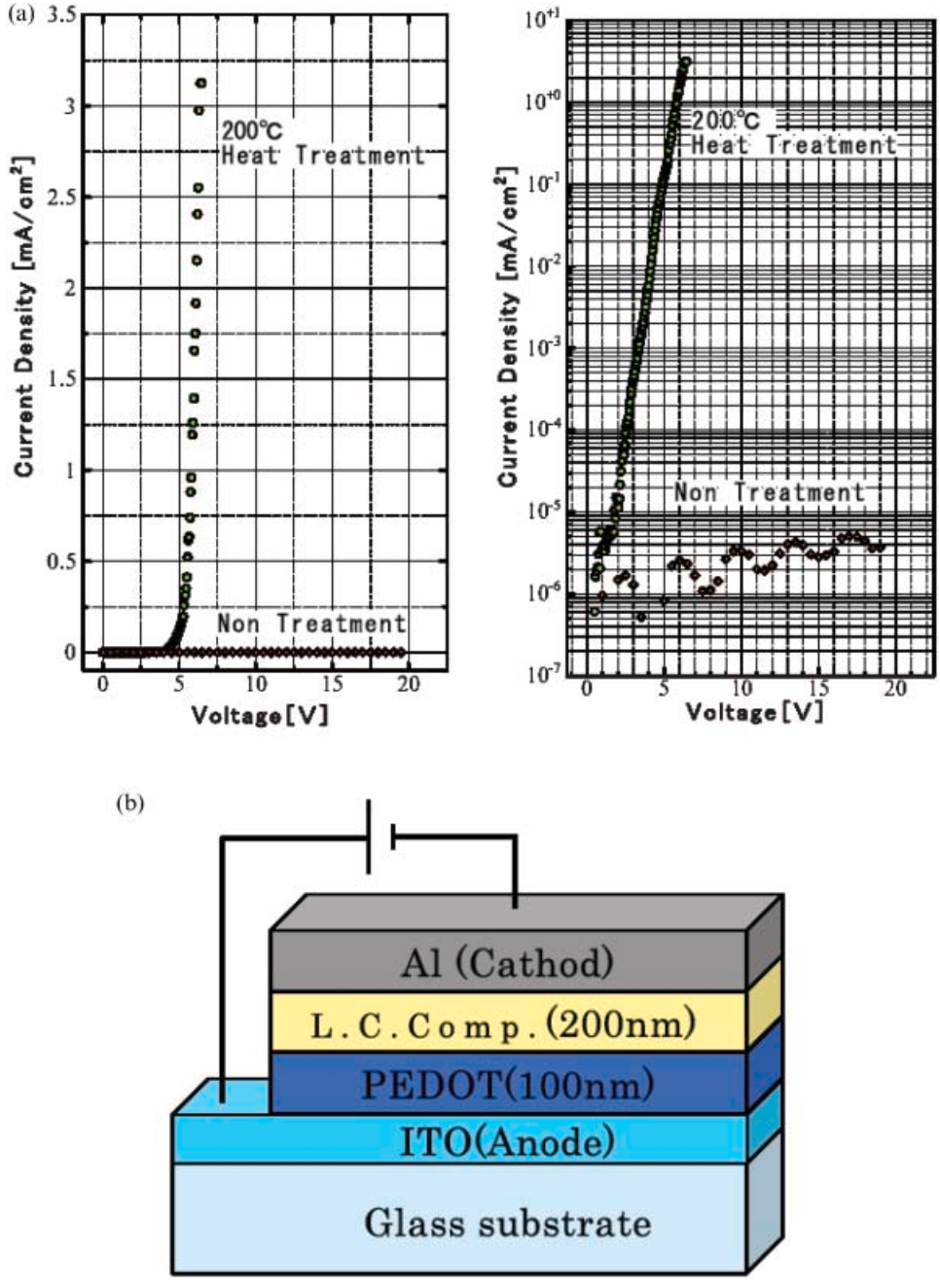

Figure 2. (a) Typical current–voltage characteristics before and after heat treatment. (b) The device structure. The electrode area is 4 mm^2. The PEDOT layer was fabricated by spin-coating.

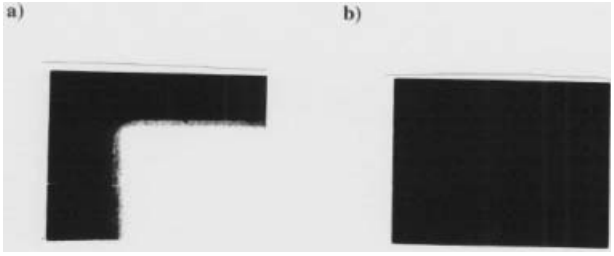

Figure 3. Photographic observation of electrical heating under the polarising microscope. (a) The sample treated at 200°C; (b) the non-heat treated sample. Since the molecular axes of the liquid crystalline sample treated at 200°C are parallel to the plane of the ITO electrode, the sample can transmit light.

small peak in the wide-angle region indicates that the lateral distance between molecules is 4.43 Å. Since the layer spacing is nearly equal to the molecular length of the synthesised compound, these compounds seem to be arranged in a monolayer (see Figure 1).

The device shown in Figure 2(b) was produced. In this device, the layer of liquid crystalline material was produced by vacuum deposition. After the deposition the device was heated to about 200°C by electrical heating under a nitrogen atmosphere to give the smectic F phase. Then it was cooled to the room temperature. An aluminium electrode was then added by vacuum deposition.

Typical current–voltage characteristics before and after heat treatment are shown in Figure 2(a). This device exhibits excellent current–voltage characteristics. A sharp threshold voltage exists. The current increases sharply at the threshold voltage for samples treated at 200°C. That is, the current increases by a factor of about $10^6 \sim 10^7$ times with an increase in voltage of 5 V. On the other hand, non-heat treated samples show an extremely low current below 1 nA and the rise of the current was not observed at about 4∼5 V. Charge transport in samples treated at 200°C is about 10^7 times larger than that in non-heat treated

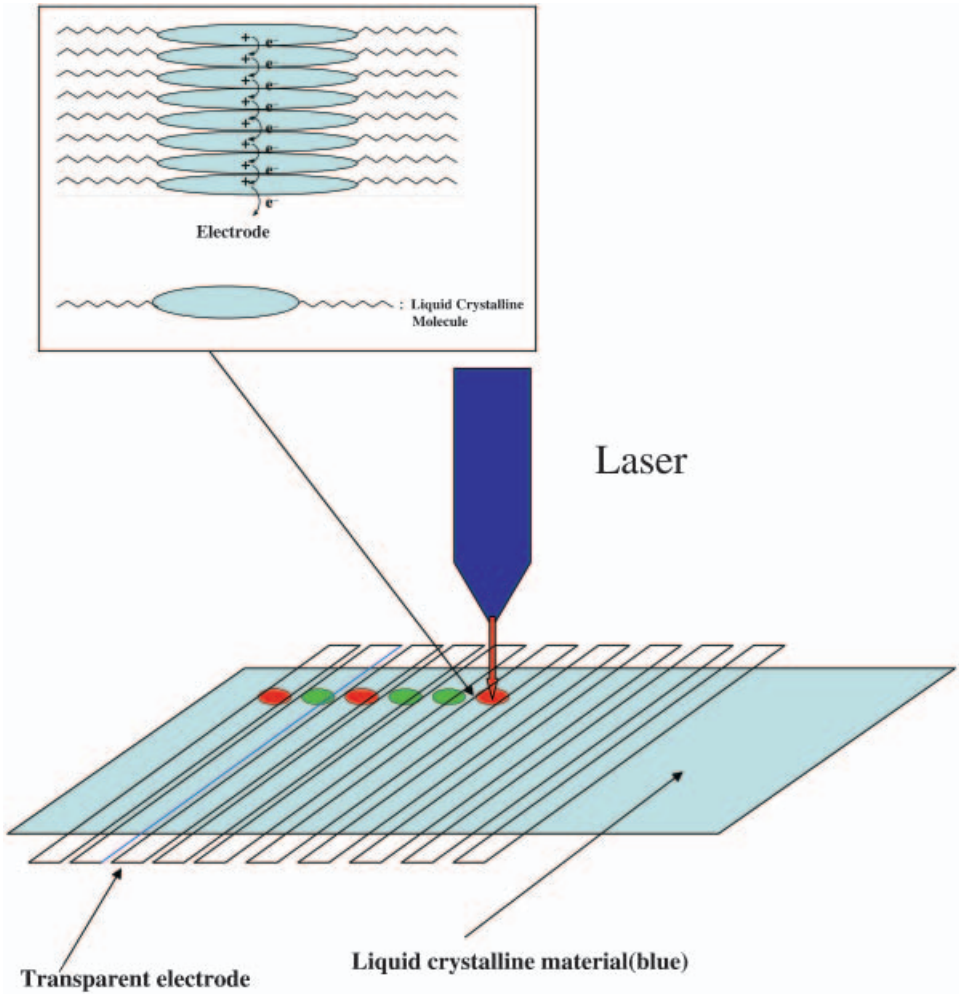

Figure 4. Principle of the new memory effect (spot heating by laser).

samples. As the molecular axes of the liquid crystal molecules of the sample treated at 200°C are parallel to the plane of the ITO electrode, the sample treated at 200°C can also transmit light (Figure 3).

This must mean that the smectic order, which was formed by the heat treatment at 200°C, was memorised after cooling to room temperature. In the system shown in Figure 4, both the spots treated by laser heating and non-treated can be read electrically by two electrodes, which sandwich the spots.

The molecular order of both the samples treated by laser heating and non-heat treated were observed under a polarising optical microscope (Figure 5). In the picture, the spot treated by laser heating is light and non-treated area is dark. This result indicates that in the spots treated by laser heating, after cooling to room temperature, the molecular axes of the liquid crystal are parallel to the plane of the ITO electrode. At about 200°C, the compounds used exhibit a smectic F phase. In the smectic F phase, the liquid crystalline molecules can move to produce the ideal order. By cooling from the smectic F phase, through the crystal smectic G phase the smectic molecular order is maintained. The crystal smectic G phase seems to remain until near room temperature because of supercooling. The strong dispersion force among the long alkyl chains may maintain the smectic liquid crystalline molecular order. The smectic liquid crystalline molecular order which was formed by the heat treatment at about 200°C seems to be memorised after cooling to room temperature.

The carrier mobility of the compound, *e*, was measured by a time-of-flight (TOF) experiment in an ITO cell (cell gap=9 μm). That is, the transient photocurrent was measured by a conventional TOF set-up consisting of a N_2 pulse laser (wavelength=337 nm, pulse duration time=600 ps, power per pulse=40 μJ), a dc power supply, a current amplifier and a digital oscilloscope.

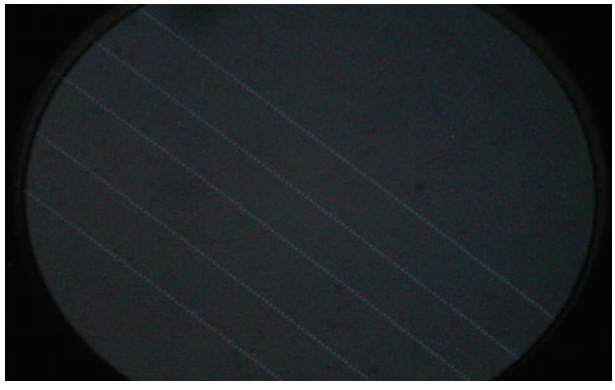

Figure 5. Spot-heat writing by a laser beam. Polarising microscope image (recorded under crossed polarisers). Semiconductor laser: 660 nm, 40 mW.

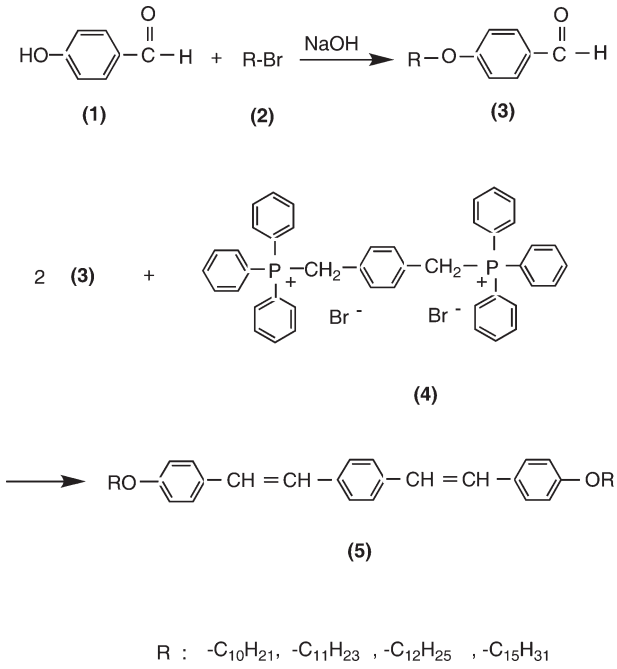

Figure 6. Synthesis of liquid crystal compounds **5**.

The hole mobilities are $1.8 \times 10^{-2}\,cm^2\,V^{-1}\,s^{-1}$ for the crystal smectic G phase (150°C) and $6.2 \times 10^{-3}\,cm^2\,V^{-1}\,s^{-1}$ for SmF phase (170°C). These values are about 1000 times larger then those of amorphous organic semiconductors. The values must be sufficient to enable use as a memory.

Therefore, this is the first new memory that can be written both by an electrical and an optical method and read both by an electrical and an optical method.

Experimental

Analysis

IR, ^{1}H NMR and mass spectra were obtained with a Hitachi 215 spectrometer, a JNM-PMX 60 spectrometer and a Hitachi M-80B spectrometer, respectively. Elemental analyses were carried out with a Carbo Erba EA 1108 instrument. The transition temperatures and mesomorphic phases were determined by means of a Mitamura Riken micro-melting point apparatus equipped with polarisers and a Mac Science DSC 3100 system. X-ray diffraction was performed with a Rigaku Rint 2100 X-ray system.

Syntheses

The compounds used were synthesised by the route shown in Figure 6. Compounds **5** are synthesised by

a Wittig reaction. Since compounds **5** are insoluble in common organic solvents, they were easy to purify. In the ^{1}H NMR spectrum, the *cis* isomer exhibits peaks around 6.6 ppm. But in this case there was no peak; therefore the *trans* isomers were obtained.

Synthesis of compound **5**.

A solution of compounds **3** (0.006 mol) and **4** (0.0025 mol) in anhydrous methanol (20 ml) was cooled to -20°C. To this was added sodium methoxide (0.005 mol) and the mixture refluxed for 10 h. The solution was cooled using an ice bath. Compound **5** was precipitated from the methanol solution. Yield 40–60%. ^{1}H NMR ($CDCl_3$): 0.8 (m, 6H, CH_3), 1.1–1.8 (m, alkyl), 3.8–3.9 (m, 4H, OCH_2), 6.9–7.5 (m, 16H, ArH, CH=CH). IR (KBr, cm^{-1}) 2800–3000 (alkyl), 1600 (Ar), 1253 (ether).

References

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