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New possibility for an organic semiconductor: a smectic liquid crystalline semiconductor having a long conjugated core and two long alkyl chains

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New possibility for an organic semiconductor: a smectic liquid crystalline semiconductor having a long conjugated core and two long alkyl chains

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We report a new possibility for liquid crystalline organic semiconductors. These materials exhibit smectic liquid crystalline phases, in which the molecules assume a smectic molecular order by self-assembly. Because of the strong dispersion force among long alkyl chains, on cooling, smectic molecular order was retained at room temperature. A charge transport ability was also retained. The conductivity of a device having smectic liquid crystalline order is about 5×10^7 that of a device with no smectic order. The current – voltage characteristic of the device has a very sharp increase at low threshold voltage (5 V). A high carrier mobility of 1.8×10^{-2} was observed in the smectic phase of one of the compounds studied (**e**).

Organic thin film transistors have attracted much attention because of advantageous features such as low cost processing, flexibility, and light weight. However, they have a few defects, such as, for example, a shallow current–voltage characteristic curve and low conductivity. There have been several studies of charge transport by liquid crystalline (LC) material, including the photoconductive behaviour of smectic LC phases [1, 2]. In the measurement of dark current of a smectic A phase, about 100 nA has been reported [1]. Dark conductivity in the nematic liquid crystalline state has also been studied, ionic conduction being dominant [3]. A nematic material was recently used as a hole injection material; it too exhibited a shallow current–voltage characteristic curve [4].

In a previous paper we reported on the dark current of phenyl piperazine-type LC compounds which have two basic nitrogens in their central core [5]. These compounds exhibited a smectic B phase and showed a dark current of 310–430 μA cm^{-2} (applied voltage 20 V, cell gap 15 μm). In this paper, we report the possibility of LC organic semiconductors using new conductive thermotropic liquid crystalline materials having a 4,4′-distyrylbenzene structure in the central core; their chemical structure is shown in figure 1. These compounds were synthesized by the route shown in figure 2. As compounds **5** are insoluble in common organic solvents, they are easy to purify. In the ^{1}H NMR spectrum, the *cis*-isomer exhibits peaks around 6.6 ppm; but here there was no peak, therefore *trans*-isomers had been obtained. These compounds have a rod-like long conjugated core and since they order in the smectic phase, this must be advantageous for the transport of charge between the long conjugated cores. These compounds exhibited dark current of 70–530 μA cm^{-2} (applied voltage 5 V, cell gap 15 μm), which is larger than values for piperazine-type LC compounds.

The mesomorphic behaviour of these liquid crystalline materials was determiend. The measurement of transition temperatures and assignment of the mesophases were carried out by means of a micro-melting point apparatus equipped with polarizers, differential scanning calorimetry (DSC), and X-ray diffraction (XRD). These compounds exhibited three smectic phases: smectic G, F, and C phases (see the table). In the XRD pattern of compound **b**, the sharp peak in the small angle region indicates a layer spacing in this smectic phase of 39.3 A; the small peak in the wide angle region indicates a lateral distance between the molecules of 4.43 A. As the layer spacing is almost equal to the molecular length of the synthesized compound, these compounds appear to be arranged in monolayers (figure 1).

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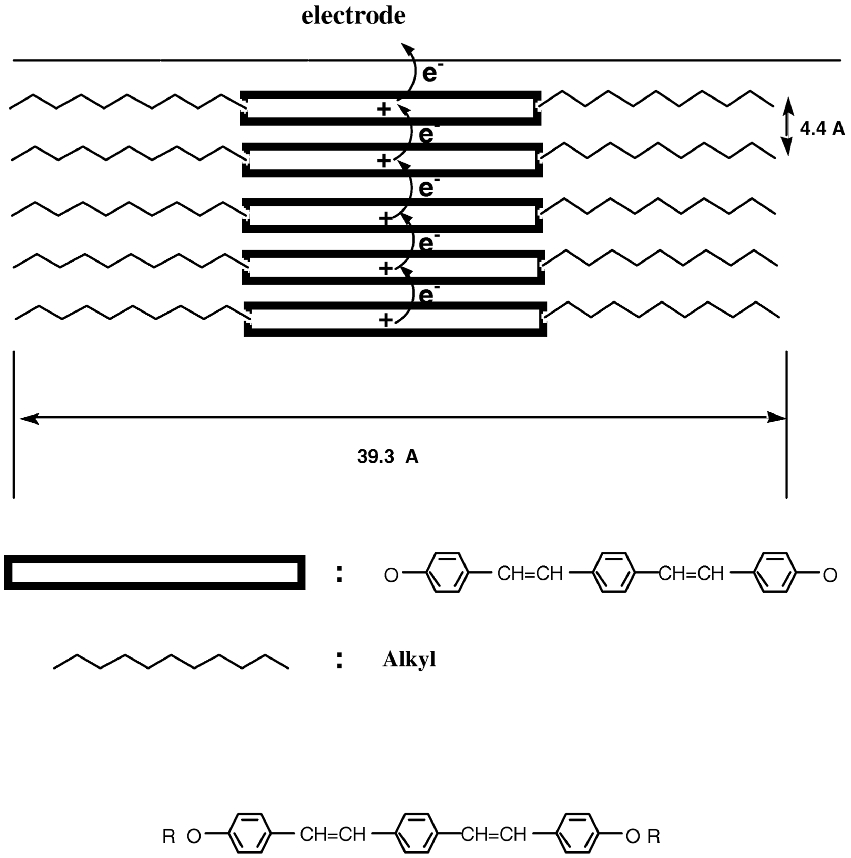

Figure 1. Chemical structure of the synthesized liquid crystalline compounds and molecular arrangement in the smectic phase.

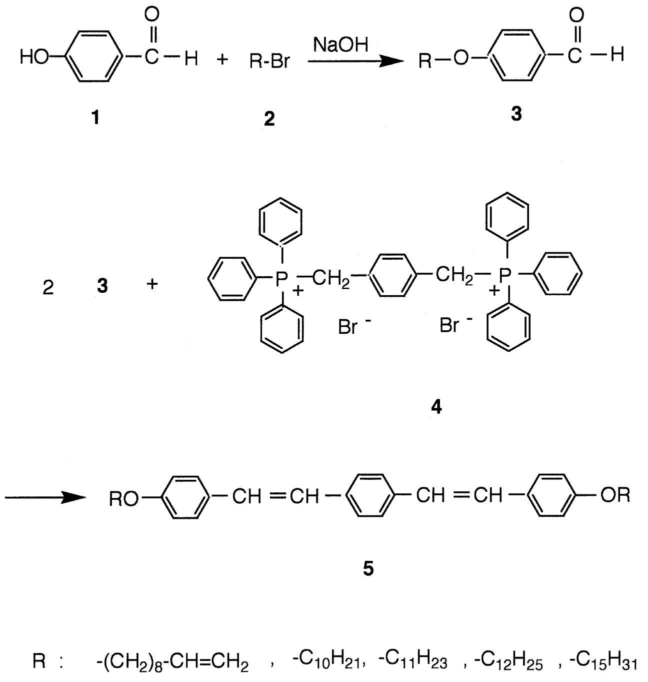

Figure 2. Synthetic pathway for the conductive liquid crystal compounds **5**.

Table. Phase transition temperatures for the new liquid crystalline compounds.

Compound	*R*	Transiton temperature/°C
a	$CH_2 = CH\text{–}(CH_2)_8$	Cr 109 SmG 181 SmF 246 SmC 252 N 267 I
b	$C_{10}H_{21}$	Cr 98 SmG 187 SmF 250 SmC 255 N 270 I
c	$C_{11}H_{23}$	Cr 138 SmG 184 SmF 247 SmC 266 N 268 I
d	$C_{12}H_{25}$	Cr 137 SmG 179 SmF 242 SmC 300 N 313 I
e	$C_{15}H_{31}$	Cr 139 SmG 160 SmF 220 SmC 246 N 248 I

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

In the device shown in figure 3 the layer of liquid crystalline material was produced by vacuum deposition. The device was then heated to 200°C under nitrogen for 10 min to give the smectic F phase; it was cooled to room temperature, and an aluminium electrode produced by vacuum deposition. Typical

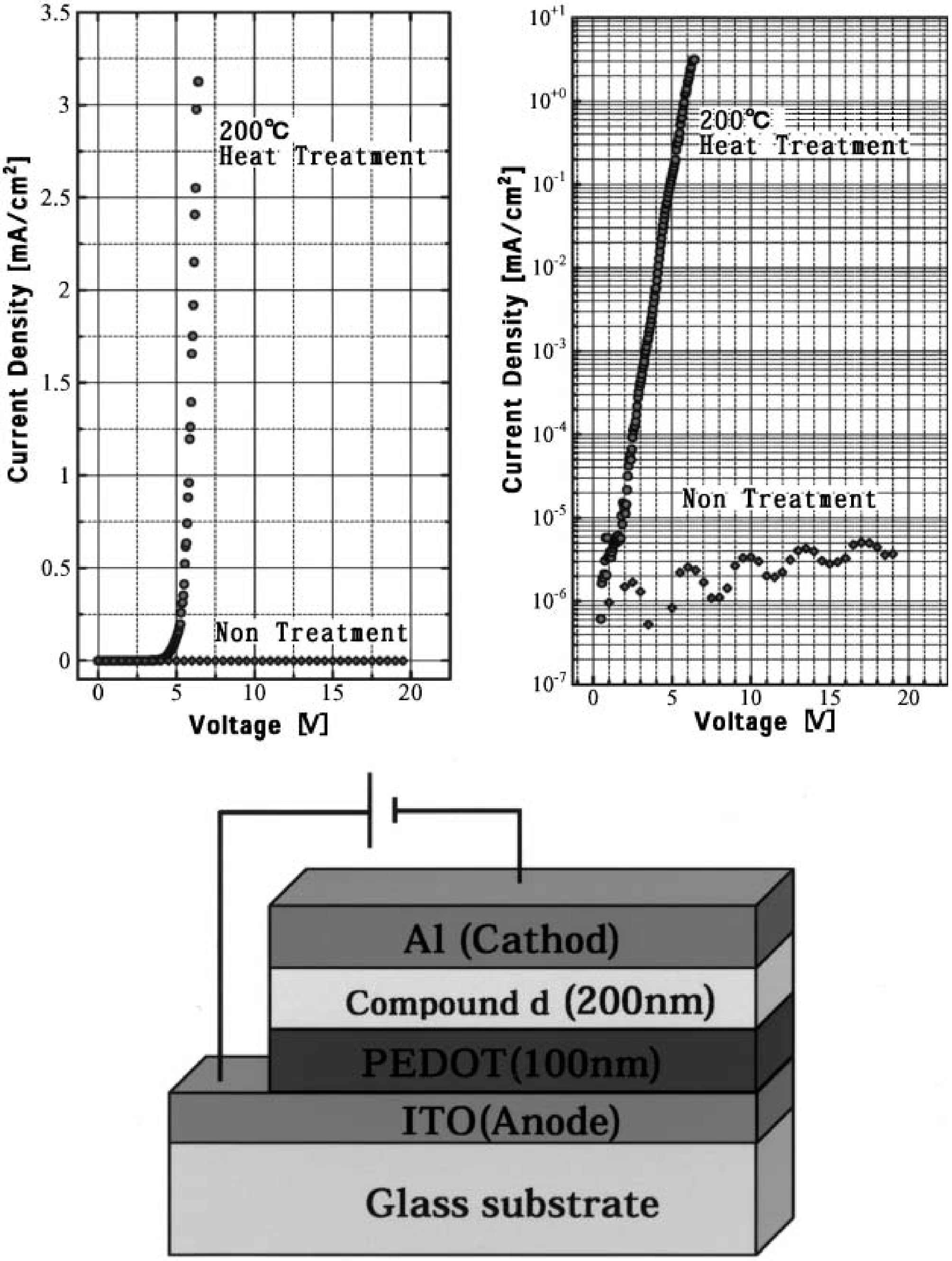

Figure 3. Typical current–voltage characteristics before and after heat treatment, and the device structure. The electrode area is 4 mm^2. The layer of PEDOT was fabricated by spin-coating.

current–voltage characteristics before and after heat treatment are shown in figure 3. The heated device exhibits an excellent current–voltage characteristic with a sharp threshold voltage. The current increases sharply at the threshold voltage for samples treated at 200°C, approaching 10^6–10^7 times with an applied voltage increase of 5 V. On the other hand, a non-heat treated sample showed extremely low current, less than 1 nA, and no rise in current was observed at 4–5 V. The charge transport capability of samples treated at 200°C is about 10^7 times that of a non-heat treated sample. Thus the smectic liquid crystalline molecular order formed by heat treatment at 200°C was retained after cooling to room temperature.

The molecular order of the sample treated at 200°C and the non-heat treated sample was observed under the

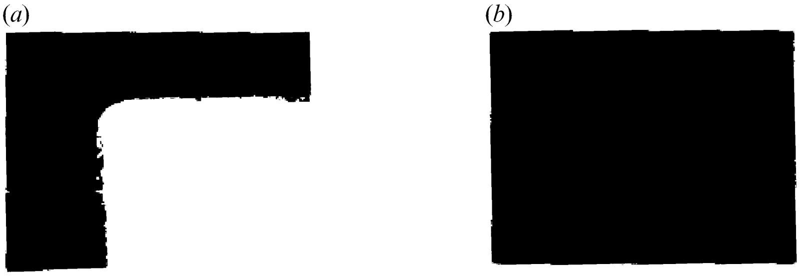

Figure 4. Polarizing photomicrographs: (*a*) sample treated at 200°C, (*b*) non-heat treated sample.

polarizing microscope, with no aluminium electrode (figure 4). In this figure, the sample treated at 200°C is light, the non-treated sample is dark. This result indicates that in the sample treated at 200°C, after the cooling to room temperature, the LC molecular axes are parallel to the plane of the ITO elecrode. At 200°C, these compounds exhibit a smectic F phase, in which the LC molecules can move to produce an ideal order. On cooling from the smectic F phase, through the smectic G phase, a true smectic molecular order is maintained. The smectic G phase is retained until near room temperature by supercooling. The strong dispersion force between long alkyl chains may hold the smectic liquid crystalline molecular order. For this reason, the smectic LC molecular order formed by the heat treatment at 200°C appears to be memorized after cooling to room temperature.

Carrier mobility of the compound **e** was measured by a time-of-flight (TOF) experiment in the ITO cell (cell gap = 9 μm). The transient photocurrent was measured by a conventional TOF set-up consisting of a N_2 pulsed laser (wavelength = 337 nm, pulse duration = 600 ps, power per pulse = 40 μJ), a d.c. power supply, a current amplifier, and a digital oscilloscope. The hole mobilities are $1.8 \times 10^{-2}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ for the SmG phase (150°C), and $6.2 \times 10^{-3}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ for the SmF phase (170°C). These values are about 1000 times larger than those of amorphous organic semiconductors.

The principal features in the use of these liquid crystalline materials as semiconductors are: (1) the 10^6–10^7 fold increase of charge transport by retention of smectic molecular order; (2) the current–voltage characteristic of a device has a very sharp increase at threshold voltage; (3) the high carrier mobility of 1.8×10^{-2} observed in the smectic phase of compound **e**. These features indicate that our conductive liquid crystalline material may be applicable as an efficient organic transistor.

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