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Strong tendency towards homeotropic alignment in a hexagonal columnar mesophase of fluoroalkylated triphenylenes

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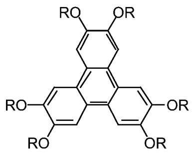
It was found that the introduction of a perfluoroalkyl group into the peripheral chains of triphenylene mesogens could provide a strong tendency towards homeotropic alignment of the hexagonal columnar ($\mathbf{Col_h}$) mesophase on a variety of substrates, indicating a new concept of molecular methodology for the alignment control of a columnar mesophase.

The alignment control of liquid crystals is an important and crucial factor in their applications. Recent studies of liquid crystals have found new properties of functionality involving the extension of the field to the plastic phase. In particular, the potentiality of fast electronic carrier transport materials is nowadays establishing a new status for mesophase materials as a new class of organic semiconductor.[1–4] However, these liquid crystals have a higher order of molecular orientation and thus tend to show a higher viscosity than lower ordered liquid crystals such as nematic and smectic A phase. In the applications of these materials in electronic devices, the alignment control of liquid crystals is essential and therefore it is required to find a useful method to obtain sufficient controllability of the molecular alignment even for such highly ordered liquid crystals.

As for discotic liquid crystals, there have been several publications on the alignment behaviour so far and well-designed controllability at the interface was successfully attained for the discotic nematic ($\mathrm{N_D}$) phase, although extreme difficulty was encountered for the rectangular columnar phase.[5–8] Recently, it was also reported that the columnar aggregates formed by hexa-*peri*-hexabenzocoronene (HBC) mesogens lie parallel to a poly(tetrafluoroethylene) surface (planar alignment), when HBC macrocycles orient orthogonal to the polymer backbone.[9] Also, the first results were obtained in the alignment control of the $\mathrm{Col_h}$ mesophase for 2,3,6,7,10,11-hexakis(n-hexyloxy)triphenylene by vibrational excitation.[10] However, it has not been known as a general molecular design principle that chemical modifications of a mesogen provide a certain controllability of the molecular alignment for a columnar mesophase without changing the mesomorphism.

On the other hand, studies of fluoro-substituted compounds have revealed that fluoroalkyl chains show a fluorophilic effect with a strong affinity to neighbouring fluoroalkyl parts, while fluorophobic interaction could work for hydrocarbon chains.[11–14] This characteristic property of fluoroalkyl groups is likely to give a tendency to form a supramolecular structure in liquid crystalline systems by microsegregation.[15–18] Recently, several homologues of a novel triphenylene derivative possessing fluoroalkylated chains were reported to show a $\mathrm{Col_h}$ mesophase with higher thermal stability.[19]

In this work, for two homologues, 2,3,6,7,10,11-hexakis-(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluorobutyloxy)triphenylene (**F1**) and the perfluoroheptyloxy derivative (**F4**), the alignment behaviour of the $\mathrm{Col_h}$ phase was investigated on the substrates modified with polyimide, cetyltrimethylammonium bromide (CTAB) and $\mathrm{InSnO_2}$ (ITO) by a polarising optical microscope and the results were compared with those of the corresponding hydrocarbon homologues (**C1** and **C4**, respectively). In consequence, it was strongly indicated that the introduction of fluoromethylene groups into the peripheral chains of discotic mesogens could easily give rise to a spontaneous homeotropic alignment in the $\mathrm{Col_h}$ phase.



F1 : R = $(CH_2)_3CF_3$
C1 : R = C_4H_9
F4 : R = $(CH_2)_3C_4F_9$
C4 : R = C_7H_{15}

compound	phase transition temperature / °C				
F1	C	132	$\mathrm{Col_h}$	171	Iso
C1	C	87	$\mathrm{Col_p}$	144	Iso
F4	C	116	$\mathrm{Col_h}$	157	Iso
C4	C	64	$\mathrm{Col_h}$	89	Iso

C: crystal, $\mathrm{Col_h}$: hexagonal columnar mesophase, $\mathrm{Col_p}$: hexagonal columnar plastic phase, Iso: isotropic liquid

F1 and **F4** were synthesised according to the method described elsewhere.[19] Commercially available CTAB and polyimide (JSR Co. Ltd., AL1254) were used without further purification. The glass substrates were cleaned with ozone cleaner before use. The polyimide-coated substrates were prepared by a spin-coating technique (1000 rpm for 1 min), followed by drying at 180 °C in air for 2 h. The CTAB-coating of a substrate was carried out by dipping the substrate into a saturated aqueous solution of CTAB, followed by drying in a stream of N_2. The mesogens were sandwiched between two modified substrates with silica beads (diameter: 2 μm) as a spacer. The textures were formed on cooling from the isotropic liquid phase and were observed under crossed polarising conditions using a polarising microscope (Olympus BH-2) in conjunction with a Mettler FP80HT hot stage.

The optical textures on the polyimide-coated substrate are shown in Fig. 1. Polyimide is widely used as a coating reagent to obtain a homogeneous alignment for rod-like liquid crystals. For discotic liquid crystals, it was reported that the discotic nematic ($\mathrm{N_D}$) phase of 2,3,6,7,10,11-hexakis(4-*n*-octyloxybenzoyloxy)triphenylene exhibits a spontaneous homeotropic alignment on the polyimide-coated substrate.[5] However, an-

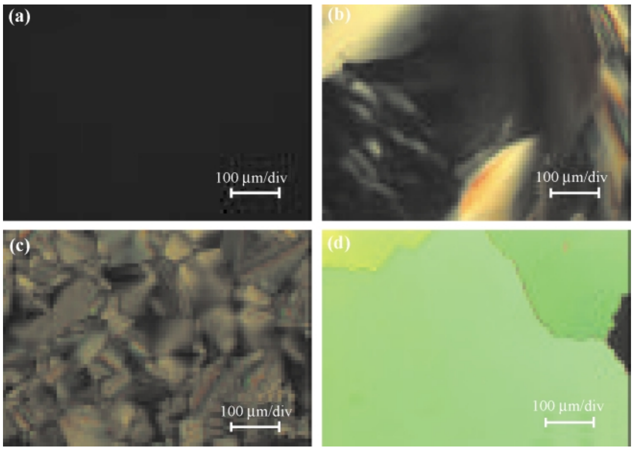


Fig. 1 Optical textures of the columnar mesophases on polyimide-coated substrate for (a) **F4** (100 °C), (b) **F1** (165 °C), (c) **C4** (80 °C) and (d) **C1** (90 °C).

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other publication states that no clear tendency towards spontaneous alignment behaviour on polyimide film could be seen with another chemical structure.[8] This indicates that the surface property is critical for lower ordered, and thus less viscous, liquid crystals like the N_D phase to determine the alignment tendency. As for the Col_h mesophase, there has been no report of alignment behaviour on polyimide film. In these texture photographs, one can easily find that **F4** spontaneously aligns in a homeotropic way on cooling from the isotropic phase, while the others do not show any clear tendency towards alignment.

The textures formed between the CTAB-coated substrates were similar to those seen for the polyimide-coated ones as shown in Fig. 2. CTAB is a typical material with which to obtain a homeotropic alignment for rod-like nematic liquid crystals. Therefore, it could be expected that a planar alignment would be obtained also for CTAB-coated substrates in the Col_h mesophase, considering the interaction between the alkyl tails of the mesogens and the surface molecules. However, a homeotropic texture spontaneously formed in the Col_h phase can be seen only for **F4**, and the others exhibit non-uniformity for the alignment.

It is surprising to observe that the textures formed between the ITO-coated substrates also show similar behaviour (Fig. 3). It is quite interesting that **F4** exhibits a strong character for spontaneous homeotropic alignment on all substrates. This indicates that the homeotropic alignment in the Col_h phase could be easily attained by the introduction of an appropriate length of fluoromethylene chains in the peripheral parts of discogens without the disappearance of the Col_h mesophase. These results seem to be reasonable, considering that the homeotropic alignment is formed to get the contacting area of the fluoro parts to the surface smaller because of fluorophobic interaction between the fluoroalkyl chains and the surface materials.

In addition, it is also interesting to see that **C1** in the Col_p phase tends to form relatively large uniform domains.

The introduction of perfluoromethylene chains into the peripheral tails of discotic liquid crystals may provide a new molecular design technique for realising a spontaneous homeotropic alignment of a Col_h mesophase.

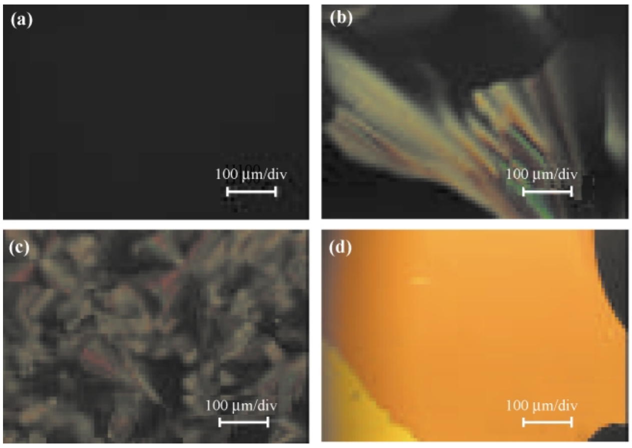

Fig. 2 Optical textures of the columnar mesophases on CTAB-coated substrate for (a) **F4** (130 °C), (b) **F1** (160 °C), (c) **C4** (80 °C) and (d) **C1** (120 °C).

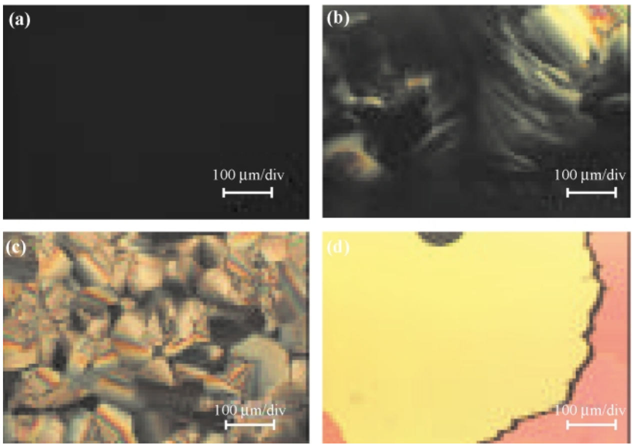

Fig. 3 Optical textures of the columnar mesophases on ITO-coated substrate for (a) **F4** (135 °C), (b) **F1** (160 °C), (c) **C4** (80 °C) and (d) **C1** (125 °C).

Notes and references

1 D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher and K. Siemensmeyer, *Phys. Rev. Lett.*, 1993, **70**, 457.
2 D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf and D. Haarer, *Nature*, 1994, **371**, 141.
3 A. M. Van de Craats, J. M. Warman, A. Fechtenkötter, J. D. Brand, M. A. Harbison and K. Müllen, *Adv. Mater.*, 1999, **11**, 1469.
4 K. Hatsusaka, K. Ohta, I. Yamamoto and H. Shirai, *J. Mater. Chem.*, 2000, **11**, 423.
5 H. Monobe, S. Mima, T. Sugino and Y. Shimizu, *Liq. Cryst.*, 2001, **28**, 1253.
6 H. Monobe, H. Azehara, Y. Shimizu and M. Fujihira, *Chem. Lett.*, 2001, 1268.
7 K. Kawata, *Chem. Record*, 2002, **2**, 59.
8 S. Ikeda, Y. Takanishi, K. Ishikawa and H. Takezoe, *Mol. Cryst. Liq. Cryst.*, 1999, **329**, 589.
9 A. M. Van de Craats, N. Stutzman, O. Bunk, M. M. Nielsen, M. Watson, K. Müllen, H. D. Chanzy, H. Sirringhaus and R. H. Friend, *Adv. Mater.*, 2003, **15**, 495.
10 H. Monobe, K. Awazu and Y. Shimizu, *Adv. Mater.*, 2000, **12**, 1495.
11 R. E. Banks, B. E. Smart and J. C. Tatlow, *Organofluorine Chemistry. Principles and Commercial Applications*, Plenum, New York, 1994.
12 M. Hudlicky and A. E. Pavlath, *Chemistry of Organic Fluorine Compounds II*, ACS Monograph 187, ACS, Washington DC, 1995.
13 D. F. Eaton and B. E. Smart, *J. Am. Chem. Soc.*, 1990, **112**, 2821.
14 C. W. Burn and E. R. Howells, *Nature*, 1954, **174**, 549.
15 W. Mahler, D. Guillon and A. Skoulios, *Mol. Cryst. Liq. Cryst.*, 1985, **2**, 111.
16 H. Kawahara, M. Hamada, Y. Ishikawa and T. Kunitake, *J. Am. Chem. Soc.*, 1993, **115**, 3002.
17 G. Johansson, V. Percec, G. Ungar and K. Smith, *Chem. Mater.*, 1997, **9**, 164.
18 G. Johansson, V. Percec, G. Ungar and J. P. Zhou, *Macromolecules*, 1996, **29**, 646.
19 N. Terasawa, H. Monobe, K. Kiyohara and Y. Shimizu, *Chem. Lett.*, 2003, **32**, 214.