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Preliminary communication
The first examples of terminally thiol-functionalized alkoxycyanobiphenyls

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In this communication, we report the synthesis of the first examples of terminally thiol-functionalized alkoxycyanobiphenyls. The thermal behaviour of these mesogens and their intermediates was investigated by polarizing optical microscopy, differential scanning calorimetry and X-ray diffractometry.

The discovery of alkyl- and alkoxy-cyanobiphenyls [1] was revolutionary in the field of liquid crystals. These cyanobiphenyls, prepared by Gray *et al.*, were the first known low melting stable nematics. They have become constituents of liquid crystal mixtures used in display technology and their various physical properties have been extensively studied [2]. In order to attach these molecules to other molecules and to prepare dimers, oligomers and polymers, a number of terminally functionalized alkoxycyanobiphenyls have been synthesized. These include bromo-, hydroxy-, amino-, carboxy-, epoxy- and olifine-terminated cyanobiphenyls [3–23]. Many interesting monomeric, oligomeric and polymeric materials have been derived from these functionalized cyanobiphenyls [24].

The interaction of thiols, disulphides and thioethers with gold is well known in the literature [25]. Both, discotic and calamitic molecules have been shown to form highly ordered self-assembled monolayers on gold-covered substrates [26]. To our surprise, while a variety of functionalized cyanobiphenyls are known, terminally thiol-functionalized cyanobiphenyls have not yet been reported in the literature. We have recently initiated a research program to attach liquid crystalline materials to gold nanoparticles [27]. Terminally thiol-functionalized mesogens are the precursor molecules for the preparation of these materials. In this communication, we report the synthesis and characterization of the first five terminally thiol-functionalized alkoxycyanobiphenyls.

The synthesis of terminally thiol-functionalized alkoxycyanobiphenyls is outlined in the scheme. Commercially available 4′-hydroxy-4-biphenylcarbonitrile was alkylated under classical reaction conditions with an excess of the appropriate α, ω-dibromoalkane to obtain the ω-brominated product **2** [3–5]. The bromo-terminated alkoxycyanobiphenyls **2** were converted to thioacetates **3** by reacting with thioacetic acid. Hydrolysis of the thioacetates furnished the desired thiol-terminated alkoxycyanobiphenyls **5**. These compounds could also be obtained by the hydrolysis of Bunte salt **4**, prepared from **2** by treatment with thiosulphate ion [28]. However, the yield was low, therefore the first thioacetate method was preferred.

All the compounds were purified by repeated column chromatography and characterized by elemental analysis and from their ^{1}H NMR, ^{13}C NMR and IR spectra. The thermal behaviour of the materials was investigated

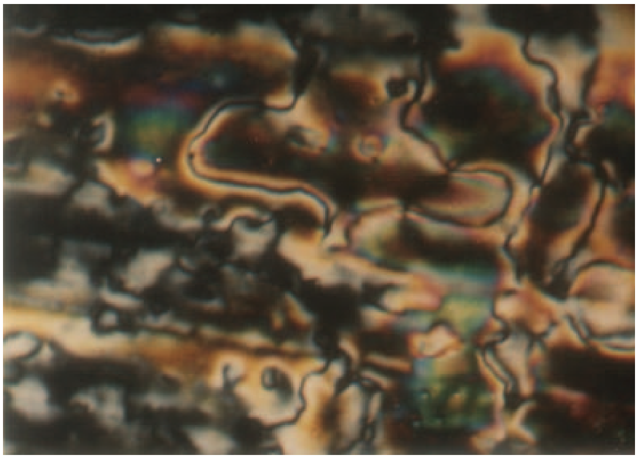

Figure. Optical texture of **5a** obtained on cooling from the isotropic liquid at 57°C (crossed polarizers, magnification ×200).

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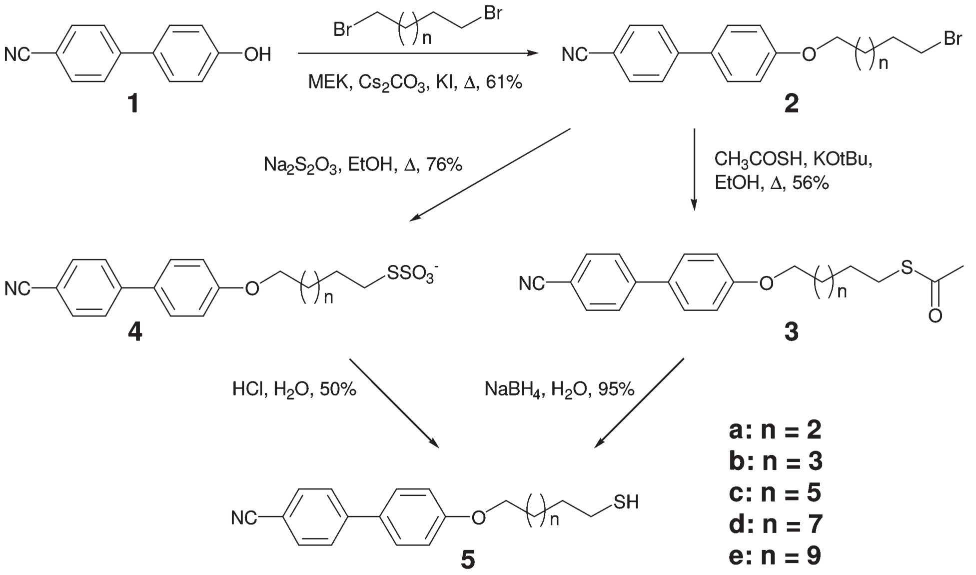

Scheme. Synthetic routes to terminally thiol-substituted alkoxycyanobiphenyls.

Table. Phase transition temperatures (peak, °C) and associated enthalpy changes (kJ mol^{-1}, in parentheses) of terminally thioacetate- and thiol-functionalized alkoxycyanobiphenyls. Cr=crystal, N=nematic phase, I=isotropic.

Compound	Heating scan	Cooling scan
3a	Cr 70.9 (27) I	I 52.4 (0.9) N 32.5 (15) Cr
3b	Cr 86.4 (41) I	I 49.8 (31) Cr
3c	Cr 78.2 (45) I	I 51.4 (39) Cr
3d	Cr 71.3 (44) I	I 63.5 (44) Cr
5a	Cr 54.9 (26) N 58.4 (0.3) I	I 57.2 (0.5) N
5b	Cr 56.0 (26) N 64.8 (0.2) I	I 63.5 (0.2) N
5c	Cr 59.3 (39) N 64.8 (0.5) I	I 63.7 (0.4) N 39.8 (28) Cr
5d	Cr and N 67.3 (46) I	I 67.0 (0.7) N 56.2 (36) Cr
5e	Cr 67.6 (3) Cr 71.6 (16) I	I 61.7 (40) N and Cr

by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The data are listed in the table.

The lower homologues of the terminally thiol-substituted cyanobiphenyl series, **5a**, **5b** and **5c**, display distinct Cr–N and N–I transition peaks in DSC. Compound **5a**, 4′-[(5-sulphanylpentyl)oxy][1,1′-biphenyl]-4-carbonitrile, on heating, melts at about 54°C to the nematic phase which clears at about 58°C. On cooling, the nematic phase appears at about 57°C (see the figure 1) and remains stable down to room temperature. The existence of the nematic phase was confirmed by X-ray measurement. Compounds **5b** and **5c** exhibit Cr–N transitions at 56 and 59.3°C, respectively. Both compounds show N–I transitions at about 65°C; on cooling, the N phase appears at about 64°C in both compounds. While the N phase of **5b** remains stable down to room temperature, the N phase of **5c** crystallizes at about 40°C. Compound **5d**, on heating under POM, shows the co-existence of N and Cr phases between 64 and 68°C before going to the isotropic phase. However, the first DSC heating run shows only a broad peak centred at 67.3°C. On cooling, the nematic phase appears at 67°C, with crystallization at 56°C. Compound **5e** on slow heating (1°C min^{-1}) shows a weak transition at 67.6°C and another endothermic transition at 71.6°C.[†] On faster heating, these peaks do not resolve and only a broad endothermic transition is observed. On cooling the isotropic phase, a metastable nematic phase is discernable by POM at 63°C. This monotropic mesophase has a high crystallization tendency which starts in the mesophase and is completed at 61°C. The first cooling DSC run shows only a broad transition centred at 61.7°C.

[†] At the time of submitting the revised manuscript, an earlier article describing the synthesis and nematic phase behaviour of this compound between 50 and 60°C was found [29].

As described already, only the nematic phase was observed in all the members of the terminally thiol-substituted cyanobiphenyl series. In contrast to the thermal behaviour of the much studied 4′-alkoxy-4-cyanobiphenyl series [30], no smectic phase is seen in the higher homologues of this series of derivatives. Similar results were reported earlier in the case of terminally hydroxy- [6–14], amino- [15] and carboxylic acid-substituted [11, 17, 18] alkoxycyanobiphenyls. The non-appearance of the smectic phase in these terminally-functionalized alkoxycyanobiphenyls has been discussed previously [9, 15]. All the new thiol-terminated alkoxycyanobiphenyls form stable monolayers on a gold surface. The full characterization of these self-assembled monolayers will be presented later.

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