Spiropyran-based liquid crystals: the formation of columnar phases *via* acid-induced spiro–merocyanine isomerisation†

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Hexagonal columnar liquid-crystalline phases are induced for a new fan-shaped spiropyran compound as the result of an acidichromism effect of spiro–merocyanine isomerisation through protonation upon incorporation of 4-methylbenzenesulfonic acid.

Columnar liquid crystals forming nano-segregated structures have drawn enormous interest recently due to their potential applications, such as for use as one-dimensional ion-, charge-, or energy-transporting media.[1–4] For example, we reported previously one-dimensional ion conduction of self-organised columnar ionic liquids.[4] For further functionalisation of such ionic materials, an approach to external stimuli-induced liquid-crystalline self-assembly[5,6] is important. Herein, we report the first example of an acid-induced thermotropic columnar liquid-crystalline assembly for a spiropyran compound, leading to one-dimensional ion transportation.

Spiropyrans are unique chemo-, thermo-, and photochromic compounds due to their external stimuli-induced spiro–merocyanine (SP–MC) isomerisation.[7,8] SP–MC transformation from the non-planar and non-ionic spiro form to the planar and ionic merocyanine form is expected to promote aggregation and formation of ordered nanostructures. Our objective is to manipulate acid-induced SP–MC isomerisation for: (i) the formation of columnar phases through self-assembly of merocyanine isomers of a spiropyran fan-shaped compound and (ii) the use of the columnar nanostructures, formed by merocyanine isomers, as the conduction path for an ion transportation. We have designed and prepared a spiropyran-based compound (**1**) with a fan-shaped trialkoxy benzene group (Fig. 1). To the best of our knowledge, neither spiropyran core columnar liquid-crystalline materials nor one-dimensional ion conductors of spiropyran derivatives have been reported.

A waxy solid of **1** was obtained by etherification of a gallic acid derivative having a 2-bromoethyl linker with 1,3,3-trimethyl-6′-hydroxy-spiro-[2*H*-1-benzopyran-2,2′-indoline].

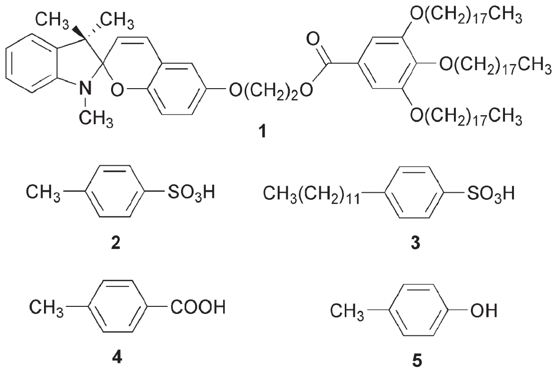

Fig. 1 Molecular structures of compounds **1–5**.

To promote mesophase formation through an acidichromism effect,[9] compound **1** was mixed with solutions of 4-methylbenzenesulfonic acid (**2**), 4-dodecylbenzenesulfonic acid (**3**), 4-methylbenzoic acid (**4**), and 4-methylphenol (**5**) (Fig. 1) which were then dried in the air overnight. Compound **2** was selected as it is one of the simplest aromatic sulfonic acids with a high melting point (106 °C). Furthermore, both compounds **2** and **3** are strong protonic acids[10,11] for stimulating SP–MC isomerisation. Compounds **4** and **5** were used to assess the effect of acidity in SP–MC isomerisation.

As shown in Table 1, compound **1** alone does not show mesomorphic behaviour as the non-planar spiro form of the molecule disturbs an ordered stacking of columnar structures.[7]

Table 1 Thermal properties of **1** and binary mixtures of **1** with **2** and **3**

Compound	Phase transition behaviour[a]/°C						
1	Cr	40 (50.1)	Iso				
1 and **2** (0.50)[b]	Cr	55 (31.5)	Cr + Col$_h$	60 (0.6)	Col$_h$	119 (0.3)	Iso
1 and **2** (0.60)[b]	Cr	56 (29.2)	Cr + Col$_h$	62 (2.9)	Col$_h$	133 (0.4)	Iso
1 and **2** (0.67)[b]	Cr	56 (81.7)	Cr + Col$_h$	63 (0.3)	Col$_h$	96 (0.3)	Iso
1 and **3** (0.50)[b]	Cr$_1$	23 (2.7)	Cr$_2$	29 (8.3)	Cr$_3$	46 (10.2)	Iso

[a] Enthalpies of transition (kJ mol^{-1}) in parentheses, determined by DSC (second heating scan, 10 °C min^{-1}). Cr = crystalline; Col$_h$ = hexagonal columnar; Cr + Col$_h$ = a biphasic mixture of crystalline and hexagonal columnar; Iso = isotropic. [b] Molar fraction of **1**, in the mixture of **1** and **2**, in parentheses.

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† Electronic supplementary information (ESI) available: Syntheses and experimental details, binary phase diagram of **1** and **2**, UV-vis spectra of each binary mixture of **1** and **3–5**, polarised optical micrographs, X-ray diffraction patterns, scheme of isomerisation process of **1**, and schematic illustration of a proposed self-assembled columnar structure of an equimolar mixture of **1** and **2**. See DOI: 10.1039/b610903a

However, an equimolar mixture of **1** and **2** leads to the formation of an enantiotropic columnar phase with the liquid-crystalline temperature ranging from 60 to 119 °C on heating. The mesophase formation can be ascribed to the acid-induced SP–MC isomerisation and the presence of the protonated merocyanine isomers.† Fig. 2 shows a polarised optical micrograph of the equimolar mixture of **1** and **2** at 90 °C on cooling. It displays a typical texture of a columnar phase. The hexagonal columnar arrangement is further confirmed by three sharp peaks at 49.1, 28.4, and 24.6 Å, corresponding to (100), (110), and (200) reflections, in the X-ray diffraction pattern obtained for the same sample at 90 °C.† A binary phase diagram of **1** and **2** has been prepared to examine liquid-crystalline behaviour of the mixtures.† The $\mathrm{Col_h}$–Iso transition curve shows a significant positive deviation, suggesting the existence of specific interactions between the two components.[12]

To confirm the presence of merocyanine and protonated merocyanine isomers upon the addition of **2**, UV-vis spectra have been obtained (Fig. 3). Prior to mixing with **2**, only the peak of the spiro isomer at 340 nm is detected for compound **1** in the bulk state (Fig. 3(a)). Upon the addition of **2**, two new peaks at 380 and 480 nm are observed for an equimolar mixture of **1** and **2** in the bulk liquid-crystalline state at 90 °C, corresponding to the absorptions of the protonated merocyanine and merocyanine isomers, respectively (Fig. 3(b)). The identification of the observed peaks is further confirmed from the UV spectrum of an equimolar mixture solution of **1** and **2** in THF, as depicted in Fig. 3(c). The absorption peak of the merocyanine isomer in the solution state is observed at 485 nm. The slight shift in the position of the merocyanine peak between the bulk liquid-crystalline state and the solution state is due to the interaction of the merocyanine isomer with the THF solvent.

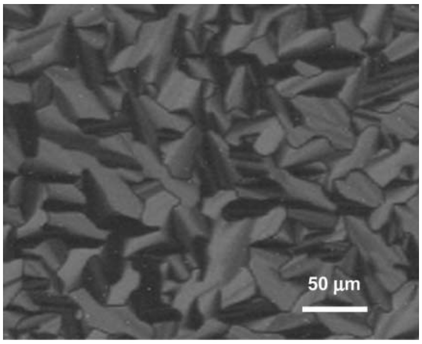

Fig. 2 Polarised optical micrograph of an equimolar mixture of **1** and **2** in the columnar state at 90 °C on cooling.

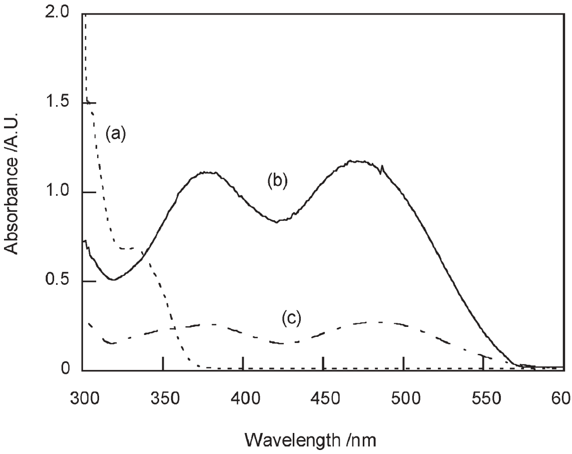

Fig. 3 UV-vis absorption spectra of (a) **1** in the bulk state, (b) an equimolar mixture of **1** and **2** in the bulk liquid-crystalline state at 90 °C, and (c) an equimolar mixture solution of **1** and **2** in THF (6.8×10^{-5} M).

Merocyanine is known to form stacked molecular aggregates.[7,13] As both merocyanine and protonated merocyanine isomers are present in the equimolar mixture of **1** and **2**, we assume that the columnar nanostructures are induced and stabilised by nanosegregation[2,14] of the lipophilic parts and the hydrogen-bonded[15] and ionic moieties.[2,16] On the other hand, when **1** is added to **3** in an equimolar ratio, no mesomorphism is observed, although both merocyanine and protonated merocyanine isomers are formed.† The long alkyl chain of **3** may disturb the packing of the merocyanines into columnar structures. In the cases of binary mixtures of **1** with **4** and **5**, respectively, neither mesomorphism nor SP–MC isomerisation is observed, which is considered to be due to their weak acidities.† These results indicate that both the acidity and the anion size of the acid are critical in promoting liquid crystal formation.

One-dimensional ion conductivities of an equimolar mixture of **1** and **2** have been examined using an alternating current impedance method with comb-shaped gold electrodes, as reported previously.[4] The self-assembled columnar polydomains are aligned in the directions perpendicular and parallel to the gold electrode *via* mechanical shearing. Fig. 4 indicates anisotropic ion conductivities for the mesomorphic mixture of **1** and **2**. The ion conductivities parallel to the columnar axis ($\sigma_{\parallel}$) for the equimolar mixture of **1** and **2** are higher than those perpendicular to the axis ($\sigma_{\perp}$) in the ordered state up to 123 °C. The highest $\sigma_{\parallel}$ value in the

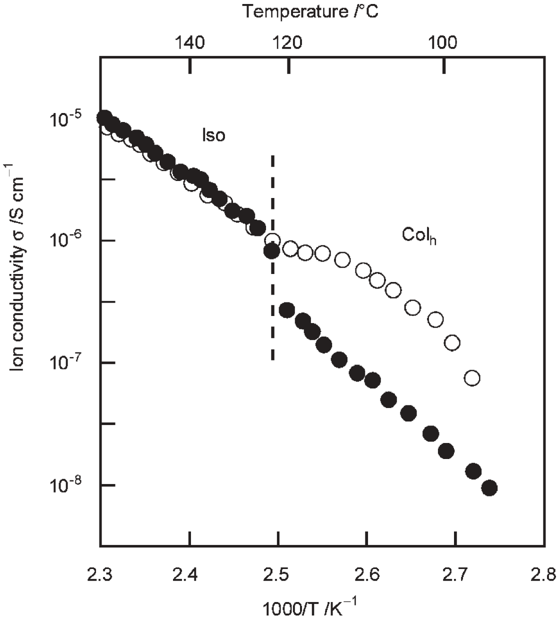

Fig. 4 Anisotropic ion conductivities of an equimolar mixture of **1** and **2** as a function of temperature on heating: (○) parallel and (●) perpendicular to the column axis. The broken line denotes the $\mathrm{Col_h}$–Iso phase transition temperature.

columnar state is 7.7×10^{-7} S cm^{-1} at 120 °C. The anisotropy ($\sigma_{\parallel}/\sigma_{\perp}$) in the ion conductivities in the columnar state is *ca.* 10. Above the Col$_h$–Iso transition temperature, the anisotropy disappears. This change indicates the formation of ion conduction pathways in the columnar state.[4] Previous reports indicated that **2** is a good proton donor[17,18] whereas **1** could serve as a proton acceptor,[19] forming the protonated merocyanine isomer. Hence, we suggest that the observed anisotropic ion conduction is due to proton hopping[20] in the phenolic moieties of the merocyanine stacks in the columnar nanostructures.

In summary, by manipulating the chemical responsiveness of a spiropyran derivative in SP–MC isomerisation, we have succeeded in developing a new hexagonal columnar mesogen. Furthermore, the new liquid-crystalline material exhibits anisotropic ion conductivities and, thus, could be developed as a novel stimuli-responsive one-dimensional ion conductor.

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