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Room temperature photochromic liquid crystal [3*H*]-naphtho[2,1-*b*]pyrans—photochromism in the mesomorphic state

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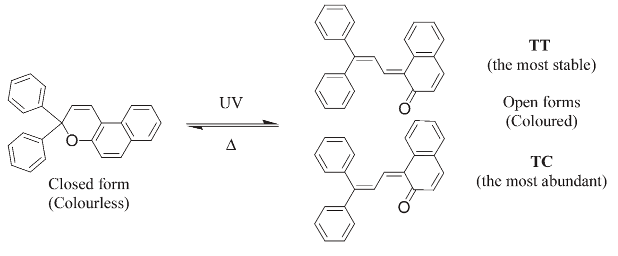
Received (in Cambridge, UK) 20th May 2004, Accepted 23rd June 2004
First published as an Advance Article on the web 2nd August 2004

Photochromic liquid crystals based on [2*H*]-chromenes functionalised in the 3,3′-positions by phenyl groups linked to 4-cyano-4′-hydroxybiphenyl groups *via* alkyl and siloxane spacers as chromophore were synthesised and the photochromic and mesomorphic behaviour was investigated.

Photochromic behaviour, the modulation of chemical structure and physical properties in molecular systems by light, is a very powerful tool in self-assembly systems with great potential in optical technological devices.[1] Photochromes based on naphthopyrans are arguably one of the most commercially successful classes of photochromic materials[1,2] (light-adjusting sunglasses), however they have so far not yet been explored as molecular materials in the context of liquid crystal systems. Irradiation (UV light) can transform a naphthopyran from the closed form (colourless form) where the phenyl groups at the 3,3′-positions are linked to the photochromic core by a C-sp^3 to the open forms (coloured forms) in which the π-conjugation length is extended through quasi-planar molecular structures. The reaction is thermally reversible and the bleaching process can be enhanced photochemically with visible light. The simplified photochromic interconversion in [2*H*]-chromene series is shown in Scheme 1.[3,4] Mesomorphic photochromes based on chromenes have to the best of our knowledge not yet been reported and indeed with very few exceptions chromenes are not photoactive in the solid state.[5] In this contribution, we report a systematic investigation of the design, synthesis, photochromic and mesomorphic properties of the first liquid crystal chromenes **5** and **6**.

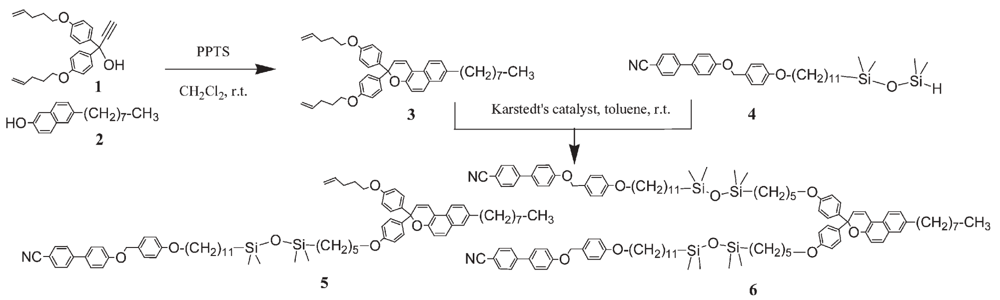
The systems **5** and **6** are connected *via* alkyl and siloxane spacers to one and two mesogens respectively. The spacers are responsible for the decoupling of the chromene and mesogenic groups. They are attached at the *para* positions of the phenyl groups located in the 3,3′-positions of the novel photochromic naphthopyran **3** shown in Scheme 2. Cyanobiphenyl group based moieties were used as mesogens, as they allow the comparison with other functional hybrid oligomeric liquid crystal systems.[6]



Scheme 1 Photochromic interconversion in [2*H*]-chromene series.

The preparation of the photochromic liquid crystals **5** and **6** is outlined in Scheme 2. The building of the intermediate chromene **3** was obtained by a "one-pot reaction" with 1,1-bis-(4-pent-4-enyloxyphenyl)prop-2-yn-1-ol **1** and 6-octylnaphthalen-2-ol **2** in the presence of a catalytic amount of PPTS. The reaction carried out in CH_2Cl_2 at room temperature yielded **3** in 75% yield.[7] The molecule **1** was synthesised classically by reacting the corresponding ketone with lithium acetylide–ethylenediamine complex in dimethylacetamide at room temperature.[8] The coupling between **3** and **4** *via* a hydrosilylation reaction with Karstedt's catalyst in toluene at room temperature afforded the LC chromenes **5** and **6** with yields of 16 and 35% respectively. The molecular structures and purity of **5** and **6** were confirmed by ^{1}H-NMR, elemental analysis and HPLC.[9]

The photochromic properties of the compounds **5** and **6** were investigated in toluene solutions and compared with those obtained for the precursor **3**, following reported procedures.[10] The introduction of cyanobiphenyl groups in **5** and **6** increases considerably the extinction coefficients in the region between 300 and 330 nm, when compared with **3**, shown in Fig. 1a. However, at the irradiation wavelength (366 nm), all the systems absorb similarly, as above 330 nm only the photochromic cores absorb. The photochromic properties of the three systems are identical when irradiated at 366 nm and the results for **3** are shown in Fig. 1b. There is no strong UV absorption (compared to **5** and **6**), thus at the investigated concentration the absorption spectrum is well defined. When photochromic solutions of **3**, **5** and **6** were irradiated at 366 nm, the solutions turned from colourless to red. The change of colour is due to the formation of the coloured forms TC and TT. The presence of the cyanobiphenyl groups does not affect the maximum absorption in the visible region. For all the molecules, the absorption maximum is centered at 482 nm and the absorbance maximum obtained at the photostationary state (equilibrium condition) at this wavelength was found to be 0.31. When the irradiation was stopped, the original absorption spectrum was recovered thermally and the bleaching kinetic monitored at 482 nm was found to be biexponential, which is typical for [2*H*]-chromenes.[4,10]



Scheme 2 Synthesis and molecular structures of LC [2*H*]-chromenes **5** and **6**

DOI: 10.1039/b407561g

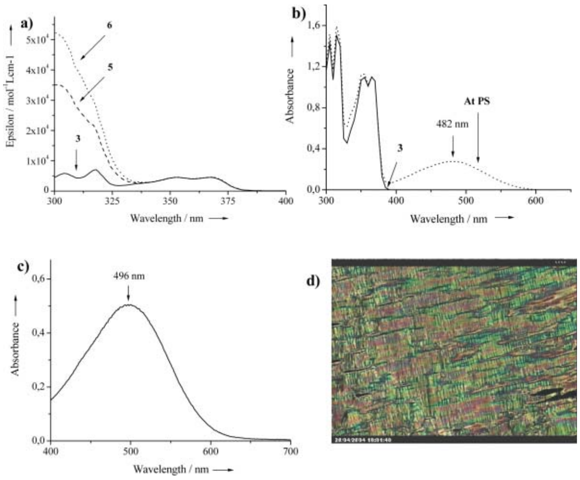


Fig. 1 **a)** Absorption behaviours of **3**, **5** and **6** in toluene solutions ($2.17\ 10^{-5}$ mol L^{-1}); **b)** absorption spectral changes of **3** under 366 nm in toluene solution ($2.17\ 10^{-4}$ mol L^{-1}); **c)** absorption of **6** under 366 nm in the mesomorphic state; **d)** OPM micrograph of **6**, supercooled to room temperature. Preferential homogeneous alignment, indication of the formation of fans (fan shaped texture), on the lower right some homeotropically aligned areas.

Table 1 Transition temperature (°C) as determined by DSC[a]

Compound	Transition temperature/°C (enthalpy/J g^{-1})				
4	Cr	35.1 (29.9)	SmA	143.9 (16.9)	Iso
5[b]	Cr	38.8 (14.1)	N	28.3 (0.22)	Iso
6	Cr	39.5 (18.4)	SmA	65.0 (0.64)	Iso

[a] Cr = crystalline, SmA = smectic A, N = nematic, Iso = isotropic. [b] Monotropic phase transition.

The resulting rate constants were 0.18 s^{-1} with an amplitude of 93% and 0.001 s^{-1} with an amplitude of 7%.

The mesogenic groups in **5** and **6** promote liquid crystalline phase behaviour, which was investigated by differential scanning calorimetry (DSC) and optical polarising microscopy (OPM). The results are listed in Table 1.

The mesogen **4** exhibits a SmA phase up to 143.9 °C, typical for molecules based on cyanobiphenyl group and terminal siloxane functions.[11] The linking of one molecule **4** to the chromene group **3** in the system **5** leads to the formation of a monotropic nematic phase (not thermodynamically stable) below 28.3 °C, characterised by a typical *schlieren* texture and a very low transition enthalpy of 0.22 J g^{-1}. The LC behaviour is stabilised for **6**, where two mesogens are linked to **3**. A SmA phase behaviour is observed in the temperature interval between 39.5 to 65.0 °C. The latter can be easily supercooled to room temperature from the isotropic liquid and a typical texture is shown in Fig. 1d. The absence of *schlieren,* the presence of black areas (the molecules are aligned perpendicular to the surface; homeotropic alignment) and the formation of fan shaped defect textures in conjunction with a higher transition enthalpy of 0.64 J g^{-1} and a low viscosity allow the assignment as a SmA phase. For the investigation of the photochromic reaction in the solid state, a sample of **6** was placed between a pair of CaF_2 slides and heated above the clearing point and than quickly cooled to room temperature. Irradiation with light at 366 nm in the solid state led to the appearance of an absorption maximum centered at 496 nm (see Fig. 1c), indicating a bathochromic shift of 14 nm when compared with the absorption maximum obtained in toluene solution (482 nm). In the solid state, the bleaching kinetic was also found to be biexponential and the resulting fading rates were found to be 0.14 s^{-1} with an amplitude of 95% and 0.001 s^{-1} with an amplitude of 5%. These results indicate a bleaching kinetic of the same order of magnitude as that obtained in toluene solution. This allows the conclusion that the photochromic reactions in the solid state are broadly similar to those obtained in solution.

In summary, we have developed novel photochromic liquid crystal [3*H*]-naphtho[2,1-*b*]pyrans where the mesomorphic properties can be tuned by the number of mesogens introduced into the photochromic core. The systems exhibit mesomorphic behaviour just above room temperature, however supercooling to ambient is possible. For the first time, the photochromic properties in the mesophase are clearly established. In such systems, the combination of photochromic and mesomorphic properties could be used as molecular ratchets, potentially very interesting in technological devices.

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9 **6** ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.01$ (s, 12 H, $SiCH_3$); .006 (s, 12 H, $SiCH_3$); 0.48 (m, 8 H, $SiCH_2$); 0.83 (m, 3 H, CH_3); 1.22–1.40 (m, 52 H, CH_2); 1.72 (m, 8 H, CH_2); 2.64 (t, $J = 7.6$, 2 H, $ArCH_2$); 3.85 (t, $J = 6.8$, 4 H, OCH_2); 3.90 (t, $J = 6.7$, 4 H, OCH_2); 4.97 (s, 4 H, OCH_2Ar); 6.13 (d, $J = 10.1$, 1 H, ArH); 6.76 (d, $J = 8.1$, 4 H, ArH); 6.86 (d, $J = 8.1$, 4 H, ArH); 7.00 (d, $J = 8.1$, 4 H, ArH); 7.07 (d, $J = 9.0$, 1 H, ArH); 7.17–7.62 (m, 24 H, ArH); 7.81 (d, $J = 8.7$, 1 H, ArH); elemental analysis calcd (%) for $C_{113}H_{148}N_2O_9Si_4$ (1790.73): C 75.79, H 8.33, N 1.56; found: C 75.65, H 8.40, N 1.57. **5** ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.01$ (s, 6 H, $SiCH_3$); 0.006 (s, 6 H, $SiCH_3$); 0.48 (m, 4 H, $SiCH_2$); 0.85 (m, 3 H, CH_3); 1.22–1.44 (m, 34 H, CH_2); 1.60–180 (m, 6 H, CH_2); 2.40 (m, 2 H, $=C–CH_2$); 2.64 (m, 2 H, $ArCH_2$); 3.85 (m, 6 H, OCH_2); 5.00 (s, 2 H, OCH_2Ar); 5.40–5.55 (m, 3 H, $H_2=H$); 6.14 (d, $J = 9.8$, 1 H, ArH); 6.78 (m, 4 H, ArH); 6.88 (m, 2 H, ArH); 7.03 (d, 2 H, ArH); 7.09 (d, $J = 8.7$, 1 H, ArH); 7.17–7.68 (m, 16 H, ArH); 7.83 (d, $J = 8.7$, 1 H, ArH); elemental analysis calcd (%) for $C_{78}H_{99}NO_6Si_2$ (1202.79): C 77.89, H 8.30, N 1.16; found: C 77.97, H 8.17, N 1.18.

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