Seminal findings in the liquid-crystal properties of bent-core molecules, such as the observation of ferroelectricity and spontaneous breaking of chiral symmetry in smectic phases composed of achiral molecules,[1–3] have broad implications for the general field of soft condensed matter. However, their practical applications[4–9] are limited because they appear only of antiferroelectric order in smectics,[12,13] or a complete structure,[16,17] they are glassy and could not be switched at room temperature. Here we show that by mixing suitable bent and rod-shape molecules one can form fluid liquid crystals at room temperature. Thus opening up a path towards possible practical applications.

We have studied binary mixtures of several rod-shape and bent-core molecules, but will focus only on those that showed complete miscibility, and provided an electrically switchable smectic phase at convenient temperature ranges. The rod-shape compound 4-n-octyloxyphenyl 4-n-hexyloxybenzoate (6OO8)[18] is one of the simplest liquid-crystal materials exhibiting nematic and tilted smectic (SmC) mesophases. The bent-core components 4-chloro-1,3-phenylene bis[4-(10-decenyloxy)benzoxy] benzoate (CIPbis10BB)[19] and 4,6-dichloro-1,3-phenylene-bis{4′-(9-decen-1-xylo)-1,1′-biphenyl}4-carboxylate (10DCIPBBC),[20] contain one and two chlorine atoms on their central rings in the 4 and 4,6 positions, respectively. This enhances their ability to form a nematic phase at relatively low, although still elevated temperatures.[19–21] In addition, they have double bonds on their terminal groups, which further decreased the nematic phase range compared to those with unsaturated chains.[22] In CIPbis10BB, which has been the subject of several studies,[23–25] the arms are relatively flexible because the outer benzene rings are separated by ester groups, whereas in 10DCIPBBC the aromatic rings of the arms are directly linked, making them much more rigid. Differential scanning calorimetry (DSC) and textural observations show complete miscibility with 6OO8 for both bent-core compounds. All mixtures have a nematic (N) phase below the isotropic (I), and in the intermediate concentration range a smectic (Sm) phase below the nematic. The I–N transition enthalpies linearly decrease from about 3 J g\(^{-1}\) to 0.7 J g\(^{-1}\) from 100% to 0% 6OO8 content, whereas the enthalpy at the transition to the induced smectic phase has a maximum of about 9 J g\(^{-1}\) at 50% which decreases to about 2 J g\(^{-1}\) at 15% and 80% 6OO8 concentrations. Control measurements involving other rod-shape materials (see Supporting Information) with a SmC (4-n-decyloxyphenyl 4-n-hexyloxybenzoate), an SmA (ethyl 4-(9-decenyloxy) biphenylcarboxylate), or N and SmA phases (bis[4-(n-butylxyloxyphenyl)cuneane-2,6- carboxylates), only showed complete miscibility and induced smectic phases for the one with SmC phase, indicating the importance of the tilted structure.

Representative polarizing microscope textures, phase diagrams, and the constituent molecules are shown in Figure 1. The nematic textures appear uniform between unidirectionally rubbed planar alignment surfaces with the optical axis parallel to the rubbing direction. On clean glass substrates and between
silane-coated surfaces they are mainly dark, indicating uniaxiality with small pretilt or weak biaxiality. The texture that appears below the nematic phase of the 80%–90% 6OO8–20%–10% CIPbis10BB mixtures is uniform, with optical axis along the rubbing direction of polyimide-coated substrates, and quasi-isotropic in homeotropic alignment conditions, proving that this is a uniaxial SmA phase.

The wide-range induced smectic phase, forming in cooling at zero electric field, has a modulated texture with the average optical axis parallel to the rubbing direction. However, when ac fields ($E > 2 \text{ V} \mu \text{m}^{-1}$, $f \sim 10–100 \text{ Hz}$) are applied during cooling, a uniform texture with optic axis parallel to the rubbing direction appears, corresponding to either SmA or antclinic SmCA phases. Between homeotropic alignment layers a grayish Schlieren texture, consisting of two and four brush defects, appears, indicating either a biaxial SmCA or SmAb structures.

To find out which is the case, we carried out layer periodicity measurements by X-ray diffraction on four different concentrations of the CIPbis10BB system at various temperatures. First of all, we have determined that the layer spacing of the uniaxial SmA phase (30.5 Å) is larger than that of the induced phase, indicating a tilted director. This, together with the textural and miscibility observations, clarifies that the biaxial smectic phase indeed has an antclinic SmCA structure (a polar SmCPA structure is excluded by polarization current measurements that showed dielectric response). The concentration dependence of the layer spacing reveals that the director tilt increases from about 15° to 30° as the bent-core component increases from 15% to 70%. Simultaneously, the height of the
Communications

peak decreases, indicating a frustration of the smectic ordering imposed by the bent-core molecules. The model structures corresponding to the experimental observations are illustrated in Figure 2b.

Electro-optical studies in the SmC_A phase reveal a significant voltage dependence of the birefringence (Fig. 3a). Although this is very similar to that observed recently in several smectic phases of pure bent core molecules,[7–9] the underlying structures and physical mechanisms are different. First, the pure bent-core SmA materials operated at much higher electric fields ($E > 5 V \mu m^{-1}$) and at much higher

Figure 2. a) Low-angle X-ray diffraction patterns of the smectic phases at four different concentrations (100%, 85%, 60%, and 30% of 6OO8 content by weight). The selected temperatures in each case are about 5 °C below the N–SmC (or the SmA–SmC for the 85% mixture) transition. The stretched length of the 6OO8 molecule is 28.7 Å which, with the measured 24.8 Å layer spacing, indicates an about 30° director tilt in the SmC phase of 6OO8. The concentration dependence of the layer spacing indicates that the tilt angle is increasing from about 15° in the SmC_a phase of the 85% 6OO8 concentration to about 34° at the 30% 6OO8 mixture. This latter value roughly corresponds to the bend angle of the bent-core compound. The measurements were done after cooling from the isotropic phases. b) Suggested model for the molecular arrangements at different concentrations of the rod-shape molecules. Thicker dotted lines indicate a more disordered smectic structure.

Figure 3. Electro-optical properties of the mixtures. a) Voltage dependence of the effective birefringence with corresponding textures for the 50% 6OO8 – 50% CIPbis10BB mixture measured at 68 °C in a 5 μm film with planar alignment coating. The data are fitted assuming two-dimensional Fredericks-type switching of the second director, as illustrated in the lower part. Rectangles indicate the tilt-plane of the bent-core and rod-shape molecules. The local coordinate system 1, 2, and 3 is chosen so that 1 is parallel to the bend direction (second director), 3 is along the layer normal (main director), and 2 is perpendicular to 1 and 3. b) Time dependence of the transmitted light intensities and textures of the corresponding states of 74% 6OO8 – 26% CIPbis10BB mixture at 65 °C (SmC_a phase).
temperatures (>100 °C). Second, in our mixtures there is a nematic phase above the smectic, which is crucial for obtaining uniform alignment. Finally, the ground states of the pure bent-core materials were found to be uniaxial (so the color tuning was attributed to field-induced biaxiality[16]), whereas our SmC⁎ phase is biaxial even without electric fields. This means that the physical mechanism of the switching of the birefringent color is different from the Langevin process proposed for the pure bent-core molecules.[19]

Owing to the smectic layer structure, the director can rotate only about the layer normal, which can be modeled as two-dimensional rotation of the unit vector along the bend direction (axis 1 on Fig. 3a) of the bent-core molecules. This motion is governed by the same equations that describe the two-dimensional Fredericks transition of the director of a uniaxial nematic liquid crystal, described by Deuling,[26] and we used this theory to fit our birefringence data. As shown in Figure 3a, the fit is excellent and gives an initial birefringence of Δn = 0.178 and a biaxiality of Δn = 0.023. The biaxiality can also be calculated by assuming that the electronic polarizability is about 0.75.

Since the switching takes place by rotation about the layer normal, it is much faster than the rotation of the director in nematic liquid crystals, and is not surprising that the measured rise time is below 0.1 ms for 1 V μm−1 fields, and the relaxation time is in the 1–4 ms range even 50 °C below the N–SmC⁎ transition. Examples of the time dependences of the transmitted intensities and the observed textures are shown in Figure 3b, where it can be seen that τrise ≈ 20 μs and τrel ≈ 0.7 ms. These rise times are comparable with those measured in SmC⁎ materials[28] and order of magnitudes smaller than in nematic liquid crystals. The relaxation time of our 5 μm film is about an order of magnitude smaller than in 1–2 μm thick nematic liquid crystals, and can be further lowered by a proper addressing technique, or by decreasing the film thickness (for example a 1 μm cell gap would provide a 25-times faster relaxation), and/or by forming a polymer network inside the film.

The fast switching speed in a wide temperature range with uniform alignment offers immediate applications. For example, to eliminate the motion blur in liquid-crystal displays (LCDs) the pixels have to be switched faster than 3 ms,[29] while the present LCD TVs offer only about 6–8 ms switching times. Our room-temperature mixtures can easily switch faster than this. In contrast to usual electro-optical switching in nematic and (anti)ferro-electric materials the switching does not involve rotation of the optic axis, but leads to variation of the birefringence several orders of magnitude larger than in calamitic liquid-crystal phases[30] and allows a 1/2 phase shift needed for black-and-white grey-scale, assuming 10 μm thick films and V ~ 10 V applied voltages. Other applications could be achieved by infiltrating these materials into photonic-crystal fibers to allow control of propagation modes and behavior within the fiber.[31] Finally, these mixtures may be used in beam steering, where the ordinary wave is varied to change the refraction angle and thus bend light away from the target.[32]

Received: January 8, 2008
Revised: February 19, 2008
Published online: