Supplementary Information

Electrically tunable color using mixtures of bent-core and rod-shape molecules

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Synthesis:

The rod-shape compound 4-n-hexyloxyphenyl- 4-n-octyloxybenzoate (*6OO8*) was synthesized by coupling the 4-n- *hexyl*oxy-phenol with the 4-n-*decyl*oxybenzoyl chloride in the presence of triethyl amine. The final product was re-crystallized several times until giving standard phase transition values of *I - 87.7 ^{o}C - N - 46.2^{o}C - SmC - 37.6^{o}C – Cr (melting: 39^{o}C)*. The control rod-shape compound with SmC phase 4-n-decyloxyphenyl 4-n-hexyloxybenzoate (*DOBHOP*) was obtained by similar way using 4-n-decyloxy-phenol and 4-n-hexyloxybenzoyl chloride. The control rod-shape compound ethyl 4-(9-decenyloxy) biphenylcarboxylate, with *Cr1 62^{o}C Cr2 76^{o}C SmE 85.9^{o}C SmA 98.7^{o}C I* phase sequence both in heating and cooling, was prepared from ethyl-4-hydroxybiphenyl carboxylic acid. This compound was reacted according to the Williamson ether formation reaction using 10-bromo-decene in the presence of dry potassium carbonate in 2-butanone applied as a solvent. After four hours reflux the reaction mixture was diluted with the water, after extraction the organic solvent was evaporated the crude product was crystallized from ethanol several times.

The control rod-shape compound bis[4-(n-butyloxyphenyl)]cuneane-2,6-dicarboxylates with *I – 143^{o}C- N- 120^{o}C – SmA- 83^{o}C – Cr* (melting: 101^{o}C) phase sequence was synthesized following the procedure described in Ref. [M1].

The first bent-core compound 4-chloro-1,3-phenylene bis[4-(10-decenyloxy)benzoyloxy] benzoate *(ClPbis10BB)* was re-synthesized following the synthetic steps described in Ref.[M2] by Julie Kim in the Synthetic Facility of the Liquid Crystal Institute of Kent State University lead by Dr. Quan Li. It exhibits a nematic phase only in cooling between 72^{o}C and 50^{o}C (melting: 88^{o}C). The other bent-core material of our studies is 4,6-dichloro-1,3-phenylene-bis[4’-(9-decen-1-yloxy)-1,1’-biphenyl]4-carboxylate *(10DClPBBC)* was prepared in the Research Institute for Solid State Physics and Optics of the Hungarian Academy of Sciences, Budapest, by the synthetic routes described in Ref. [M3]. It has an enantiotropic nematic phase with I *97.4^{o}C N 55^{o}C Cr (melting: 57^{o}C)* phase sequence.

The purity of the samples was checked by high performance liquid chromatography (HPLC) using a Merck-Hitachi chromatograph equipped with a Merck RP18 column (Cat. No 16051).

Mixture preparations:

Making mixtures to tailor the properties of liquid crystal materials is a well-developed technique; in fact, liquid crystal displays usually contain over five different types of molecules. In general however, it is very difficult to predict the properties of the mixtures just by looking at the constituent molecules and their phase behaviors. To see the miscibility trends first ‘contact preparation’ cells were made. This was achieved by capillary filling the pure components in their isotropic phase from the opposite sides of the empty cells. First the component with higher clearing point was filled in half way, and then the other component was filled in. After their fronts met, the sample was heated to the isotropic phase allowing the components to diffuse together, thus providing a smooth gradient of concentrations. If the components showed complete miscibility, mixtures a number of different uniform concentrations were made by weighing the components using a microbalance (Perkin Elmer AD-6) and mixing them thoroughly in their isotropic liquid phases. The uniformity of the mixtures was checked by DSC and textural observations.

Cell preparations:

Liquid crystal test cells used for planar alignment were purchased from E.H.C Co., Ltd., Japan. These cells (5-8μm thicknesses) were made of glass substrates with uni-directionally rubbed polyimide coatings.

Cells made using clean microscope slides with cover glass were used without spacers.

For the cells used for in-plane switching a 7''x7''x0.120'' chrome on glass positive photomask was designed using AutoCad. Two types of arrays of 8x10 cells with 5mm x 5mm active areas were fabricated in the clean room at the Liquid Crystal Institute of Kent State University by Indium Tin Oxide (ITO) etching. One array had only 5mm x 5mm single pixels, while the other one comprised of interdigitated electrode pattern with 5μm, 7.5μm and 10μm spacing between in-plane electrodes. After ITO patterning, the substrates were coated with either planar (aligns director parallel to the substrate) or homeotropic (aligns the director perpendicular to the substrate) alignment layers. For planar alignment a polyimide film was used by spin-coating, then by soft-baking for 2min at 90°C, hard-baking for 1hr at 230°C. These substrates were used either without rubbing, or after uni-directionally rubbed five times using a piece of velvet cloth. The rubbing was either along, perpendicular or 45° away from the in-plane electrodes and the substrates were put together with the rubbing directions antiparallel with one another. The homeotropic cells were coated with *n-octadecyltriethoxysilane* (ODS). For cell thickness uniformity, micro-pearl type ball spacers (from Sekisui Co.) were used. The empty cell thicknesses were measured by analyzing the interference spectra obtained using UV-VIS spectrophotometer (USB2000, OceanOptics Inc.) and thicknesses varied between 3.5μm and 6μm.

Phase characterizations

The characterization of liquid crystalline phases and phase transitions were done by textural observations using a polarizing microscope in conjunction with Differential Scanning Calorimetry (DSC) and X-ray diffraction.

Textural observations were made by using a Polarizing Optical Microscope (BX60 from Olympus). The liquid crystal samples were placed in a computer controlled precision Hot Stage

(*STC200F* from INSTEC) that regulated the temperature with a resolution better than 0.1°C. The microphotographs of the textures were captured using a Sony CCD camera. The transmitted light intensity was integrated over 1mm areas by a biased photodiode (U.O.T-455Hs from Oriel) placed in the eye piece of the polarizing microscope. The temperature dependences of the light intensity, recorded using a Digital Multimeter (HP 34401A), were used to identify the phase transition signatures.

DSC measurements were carried out by Perkin Elmer DSC 7 under 2°C/min heating/cooling rates.

For the **small angle X-ray measurements** the scattering of Ni-filtered Cu K_α radiation (λ = 1.542 A) was recorded using a Kratky Compact camera (Anton Paar, Graz, Austria) supplied with a position sensitive detector (M. Braun, Garching, Germany). The primary beam was line focused; therefore the intensity curves were corrected considering the geometry of the beam profile using the indirect method described by Glatter [M4]. The samples were transferred into thin walled quartz capillaries (Heidelberg, Germany) with a diameter of 1 mm.

Switching time and electric current measurements:

Electric fields were applied from an Arbitrary Waveform Generator (HP 33120A) and amplified by an FLC F20AD Voltage Amplifier. Time dependence of the transmitted light intensity integrated over 1mm area by a biased photodiode (U.O.T-455Hs from Oriel), placed in the eye piece of the BX60 polarizing optical microscope, was recorded by a Digital Oscilloscope (HP 54600B) to measure the switching time. The electric currents were recorded with the same oscilloscope in form of the voltage drop across a 0.2-20kΩ resistance placed in series with the liquid crystal sample.

Birefringence measurements:

The birefringence and its change under electric fields were quantitatively measured by analyzing the transmission spectra, and by the Senarmont method.

The transmitted intensity was measured between crossed polarizers with the sample whose optical axes were aligned 45^{o} to polarizer axes. This system has a relationship described by $I \propto \sin^2\left(\frac{\pi \Delta n d}{\lambda}\right)$ where d is the sample thickness, λ is the wavelength of light, and Δn is the measured birefringence. This intensity behavior for a given wavelength usually has a π degeneracy (called modes) related to the sinusoidal behavior of the model, however by fitting the spectra we could determine the birefringence, which mode we were in and the change due to applied electric fields.

In the Senarmont method linearly polarized light from a Helium-Neon laser is sent through a birefringent material, emerging elliptically polarized. A quarter-wave along with the sample changes the polarization of the light from linear to elliptical. Intensity data is recorded using a Newport 8184G photo detector as the analyzer rotates its principle axis Θ by 360°. The resulting curve fits the equation $\frac{I}{I_0} = \frac{1}{2} - B\cos\left(2\Theta\right)$ where $B = \frac{1}{2}\sin\delta$ and $\delta = \frac{2\pi \Delta n d}{\lambda}$. This process was repeated for different applied voltages ranging between $0.3V_{rms}$ to $20V_{rms}$.

Data analysis and fitting:

The software package MatLab was used to create a series of least squares fitting programs of the average birefringence in the material. The numerical minimization methods used were built-in functions of Matlab, *'fminsearch'* and *'fminbnd'*. The '*fminbnd'* algorithm is based on golden section search and parabolic interpolation and can only solve for a single variable. The *‘fminsearch’* uses the simplex search method described in Ref. [M5]. This is a direct search method that does not use numerical or analytic gradients.

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