Supporting Information

Study of ferro- and anti- ferroelectric polar order in mesophases exhibited by bent-core mesogens

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1. Dielectric spectroscopy calculations

In order to understand the nature of the dielectric relaxation modes, the frequencydependent dielectric loss $\varepsilon''(f)$ curves have been fitted by Havriliak-Negami (H-N) fit function with an additional term standing for the low-frequency conductivity contribution as follows:

$$\varepsilon'' = \frac{\sigma_0}{(2\pi f)^s} + \sum_{k=1}^N \frac{\delta \varepsilon_k \sin(\beta \theta)}{\left[1 + (2\pi f \tau_k)^{2\alpha_k} + 2(2\pi f \tau_k)^{\alpha_k} \cos(\alpha_k \pi/2)\right]^{\beta/2}}$$
(1)

with $\theta = \tan^{-1} \left[\frac{(2\pi f \tau_k)^{\alpha_k} \sin(\alpha_k \pi / 2)}{1 + (2\pi f \tau_k)^{\alpha_k} \cos(\alpha_k \pi / 2)} \right]$

where $\delta \varepsilon_k$ is the dielectric strength, ε_{∞} is the high-frequency limit of the permittivity, τ_k (= 1/2 πf_k) is the relaxation time, f_k is the corresponding relaxation frequency, α_k and β_k are the shape parameters (can be between 0 and 1) describing the symmetric and non-symmetric broadness of dielectric dispersion curve, respectively and *k* is the number of relaxation processes. However, σ_0 is related to the DC conductivity and *S* is a fitting parameter responsible for the slope of the conductivity.



Figure S1. Frequency dependence of the imaginary (ε'') parts of the permittivity at different temperatures for compound 1/7: in (a) HG or planar and (b) HT or homeotropic sample configurations.



Figure S2. Frequency dependence of imaginary (ε'') parts of permittivity for the compound 1/7 at a particular temperature: in (a) HG or planar and (b) HT or homeotropic sample configurations. Solid curves represent different relaxation modes obtained after fit to data points with H-N equation.



Figure S3. Frequency dependence of the imaginary (\mathcal{E}') parts of the permittivity at different temperatures for compound 1/9: in (a) HG or planar and (b) HT or homeotropic sample configurations.



Figure S4. Frequency dependence of imaginary (ε'') parts of permittivity for the compound **1/9** at a particular temperature: in (a) HG or planar and (b) HT or homeotropic sample configurations. Solid curves represent different relaxation modes obtained after fit to data points with H-N equation.



Figure S5. Frequency dependence of the imaginary (\mathcal{E}') parts of the complex permittivity at different temperatures for compound 1/10: in (a) planar and (b) homeotropic oriented samples.



Figure S6. Frequency dependence of imaginary (ε'') parts of permittivity for the compound 1/10 at a particular temperature: in (a) HG or planar and (b) HT or homeotropic sample configurations. Solid curves represent different relaxation modes obtained after fit to data points with H-N equation.

3. Electro-optical study

With an application of an square wave of voltage 180 V_{PP} and frequency 5 Hz, the optical textures were observed in ITO coated cells with planar and homeotropic alignments.



Figure S7. Optical textures of the compound **1/9** and **1/10** for an applied square wave AC voltage at different mesophases; (a-c): compound **1/9** in HG cell, (d-f): compound **1/9** in HT cell, (g-j): compound **1/10** in HG cell, (k-n): compound **1/10** in HT cell. Crossed arrows indicate the direction of the analyzer and polarizer. Red arrows define the rubbing direction in planar orientations.