SUPPLEMENTARY INFORMATION

Thermotropic reentrant isotropy and induced antiferroelectricity in the ferroelectric nematic realm: Comparing RM734 and DIO

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Abstract

The current intense study of ferroelectric nematic liquid crystals was initiated by the observation of the same ferroelectric nematic phase in two independently discovered organic, rod-shaped, mesogenic compounds, RM734 and DIO. We recently reported that the compound RM734 also exhibits a monotropic, low-temperature, antiferroelectric phase having reentrant isotropic symmetry (the I_R phase), the formation of which is facilitated to a remarkable degree by doping with small (below 1%) amounts of the ionic liquid BMIM-PF_6. Here we report similar phenomenology in DIO, showing that this reentrant isotropic behavior is not only a property of RM734 but is rather a more general, material-independent feature of ferroelectric nematic mesogens. We find that the reentrant isotropic phases observed in RM734 and DIO are similar but not identical, adding two new phases to the ferroelectric nematic realm. The two I_R phases exhibit similar, strongly peaked, diffuse x-ray scattering in the WAXS range ($1 < q < 2$ Å^{-1}) indicative of a distinctive mode of short-ranged, side-by-side molecular packing. The scattering of the I_R phases at small q is quite different in the two materials, however, with RM734 exhibiting a strong, single, diffuse peak at $q \sim 0.08$ Å^{-1} indicating mesoscale modulation with ~80 Å periodicity, and DIO a sharper diffuse peak at $q \sim 0.27$ Å^{-1} ~ (2π/molecular length), with second and third harmonics, indicating that in the I_R phase of DIO, short-ranged molecular positional correlation is smectic layer-like. The I_R phases are metastable, eventually crystallizing.

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SECTION S1 *– MATERIALS AND METHODS*

The mixtures were studied using standard liquid crystal phase analysis techniques, previously described [1, 2,3,4,5] including depolarized transmission optical microscopic observation of LC textures and response to electric field, x-ray scattering (SAXS and WAXS), and techniques for measuring polarization and determining electro-optic response [4].

Materials – DIO (2,3′,4′,5′-tetrafluoro-[1,1′-biphenyl]-4-yl 2,6-difluoro-4-(5-propyl-1,3-dioxane-2-yl)benzoate, ***Fig. S1,*** compound ***3***) is a rod-shaped molecule about 20 Å long and 5 Å in diameter, with a longitudinal electric dipole moment of about 11 Debye. DIO was first reported by Nishikawa et al. [6] and was synthesized by the Walba group as described in [4]. The synthesized compound was found to melt at T = 173.6°C and in addition to a conventional nematic (N) phase, exhibited two additional mesogenic phases, a lamellar antiferroelectric (the SmZ_A) and the ferroelectric nematic (N_F). The transition temperatures on cooling were Iso – 173.6°C – N – 84.5°C – SmZ_A – 68.8°C –N_F – 34°C – X, very similar to the temperatures reported by Nishikawa.

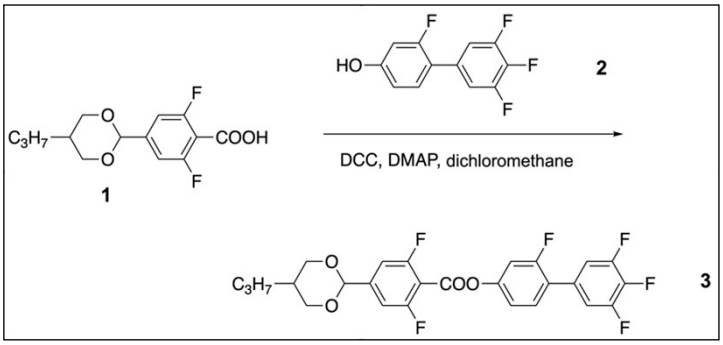

Figure S1: Synthesis scheme for DIO.

EMIM-TFSI {1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide} was obtained from Millipore/Sigma and used without further purification.

Methods – Obtaining the I_R^{lam} phase in undoped DIO or DIO/IL mixtures – Samples of DIO and its mixtures with ionic liquid were heated into the N phase at 120°C before they were loaded into capillaries or liquid crystal cells. After filling, the x-ray capillaries were quenched on a flat metal surface at T = -19°C, by which means the entire volume of the doped LC rapidly transitioned to the optically transparent reentrant isotropic phase. No annealing was required. The capillaries were then heated back to room temperature to carry out x-ray diffraction in the dark phase, after which they were heated to the uniaxial nematic phase and cooled at -0.5°C per minute to selected temperatures where x-ray diffraction measurements of the N and SmZ_A phases were carried out. In the EMIM/DIO mixtures, crystals of DIO typically started to appear when the sample was cooled to between 50°C and 40°C, making it challenging to obtain diffraction images of the N_F phase. The capillary could subsequently be reheated to the nematic and quenched to the I_R phase as many times as desired.

The phase transition temperatures in cells and capillaries were determined using depolarized transmission optical microscopy while cooling the samples at -0.5°C per minute. DIO crystals typically started to nucleate and grow at around 40°C in such temperature scans. In order to favor formation of the I_R^{lam} phase rather than the crystal, it is necessary to cool the samples quickly, which prevents the crystal phase from growing to cover the whole volume before the transition to the I_R^{lam} phase can take place. For example,

crystallization could be suppressed by cooling at -3°C per minute, by which means a cell with the I_R phase filling the entire volume could be obtained. In order to measure the precise temperature of the $N_F - I_R$ transition, the cell was first quenched to 30° C and then cooled at -0.5° C per minute to the transition at about 27°C.

The I_R^{lam} phase in the DIO/EMIM mixtures is apparently less thermodynamically stable than the crystal. At 20°C, the crystal phase was typically observed to start nucleating following overnight storage. However, the I_R^{lam} phase was stable for at least five days if the sample was held at 9°C. Upon heating at 0.5°C per minute, the I_R^{lam} phase transitioned to the N_F phase at $T \sim 45$°C, after which crystals quickly grew in the sample.

X-ray scattering – For SAXS and WAXS experiments, LC samples were filled into thin-wall capillaries 0.7 to 1 mm in diameter. Data presented here are powder averages obtained on cooling using a Forvis microfocus SAXS/WAXS system with a photon energy of CuK_α 8.04 keV (wavelength = 1.54 Å). Each scan took ~1 hr at a given temperature.

Polarized light microscopy – Optical microscopy of LC cells viewed in transmission between crossed polarizer and analyzer, with such cells having the LC between uniformly spaced, surface-treated glass plates, provides key evidence for the macroscopic polar ordering, uniaxial optical textures, and fluid layer structure in LC phases and enables direct visualization of the director field, $\boldsymbol{n}(\boldsymbol{r})$, and, apart from its sign, of $\boldsymbol{P}(\boldsymbol{r})$.

Electro-optics – For making electro-optical measurements, the mixtures were filled into planar-aligned, in-plane switching test cells (Instec, Inc.) with unidirectionally buffed alignment layers arranged antiparallel on the two plates, which were uniformly spaced 3.5 μm apart. In-plane ITO electrodes on one of the plates were spaced by a 1 mm wide gap and the buffing was along a direction rotated 3° from parallel to the electrode edges. Such surfaces give a quadrupolar alignment of the N and SmZ_A directors along the buffing axis and polar alignment of the N_F at each plate, leading to a director/polarization field in the N_F phase that is parallel to the plates and has a π twist between the cell surfaces [3].

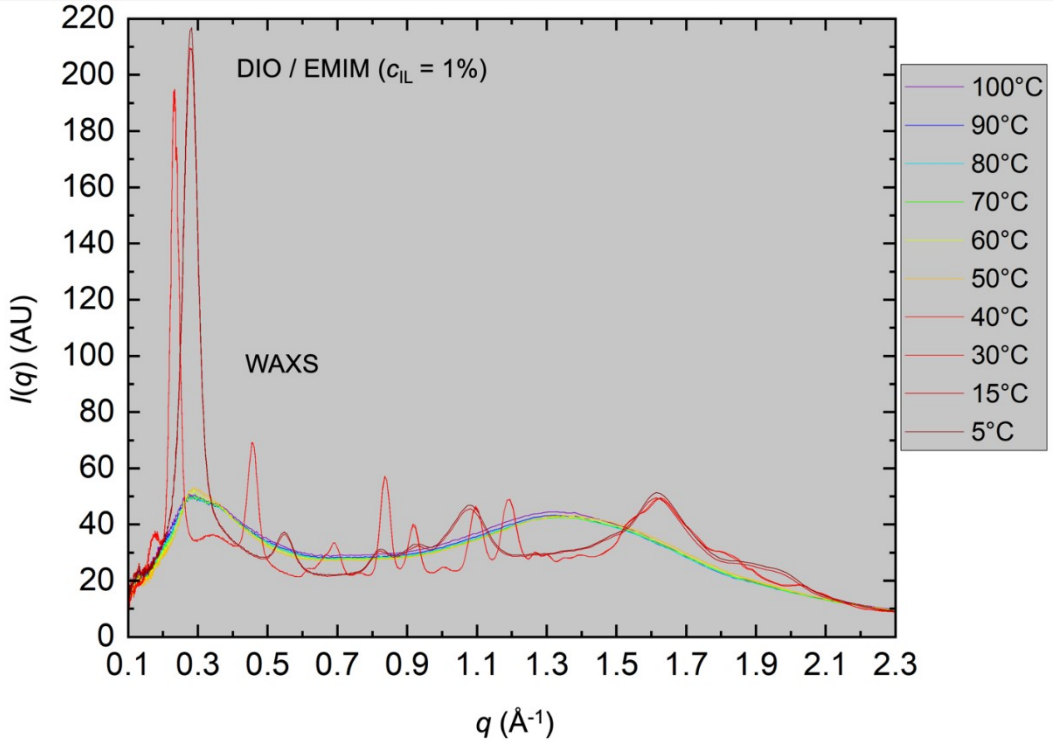

Figure S2: WAXS scans vs. T of a DIO/EMIM (c_{IL} = 1%) mixture. Diffraction measurements were made first in the L_{α}^{lam} phase, on heating from 5°C to 15°C. The

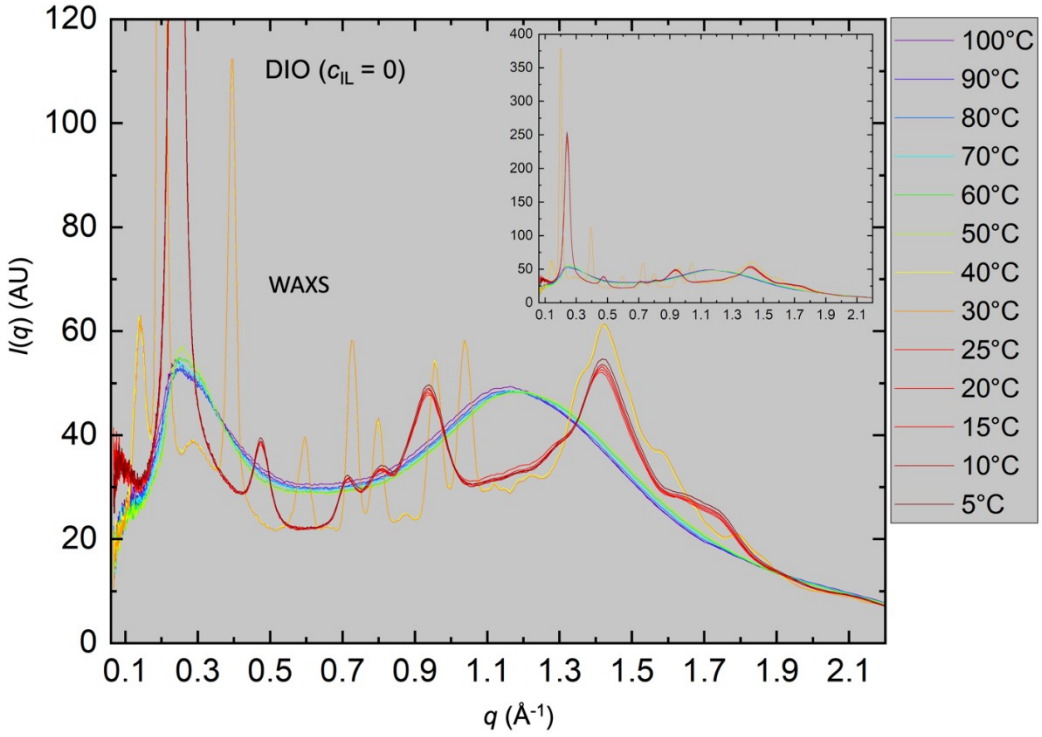

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Figure S3: WAXS scans vs. *T* of undoped DIO. Diffraction measurements were made first in the I_A^{lam} phase, on heating from 5°C to 25°C. The sample was then heated to the nematic phase at 100°C, and the remaining measurements were carried out on cooling to 30°C. The sample crystallized below 50°C.

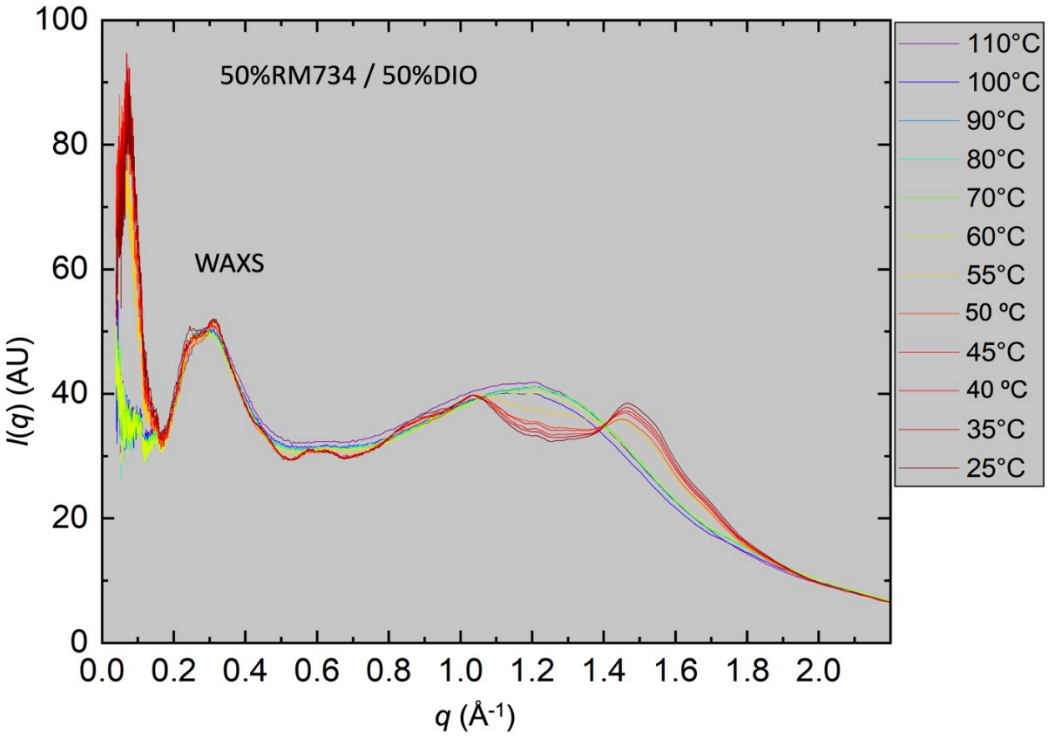

Figure S4: WAXS cooling scans vs. *T* of a 50% RM734/50% DIO mixture.

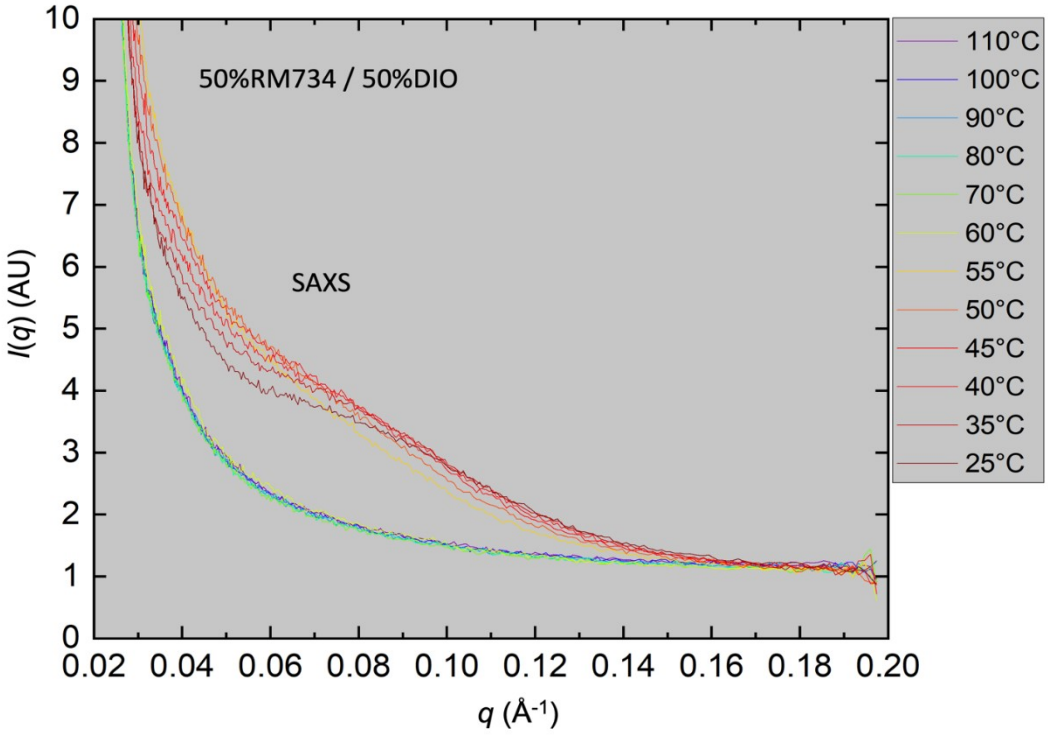

Figure S5: SAXS cooling scans vs. *T* of a 50% RM734/50% DIO mixture.

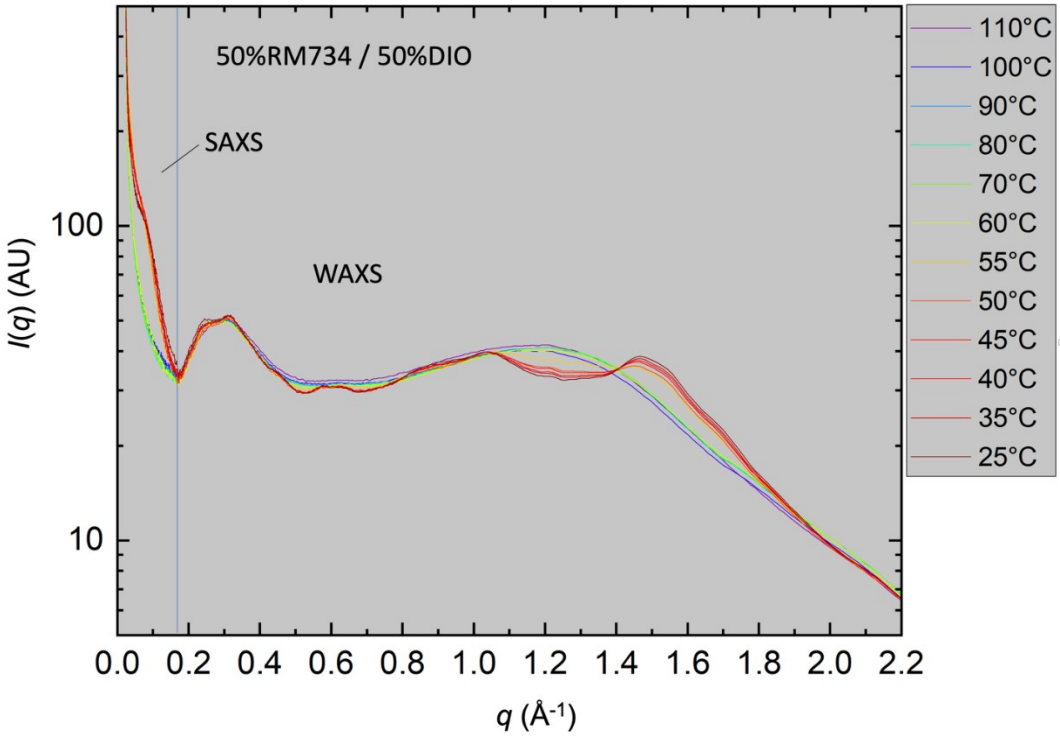

Figure S6: SAXS & WAXS cooling scans vs. *T* of a 50% RM734/50% DIO mixture.

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