Supporting Information

to

Polarization loss in the organic ferroelectric trialkylbenzene-1,3,5tricarboxamide (BTA)

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1 – GIWAXS data

X-Ray Diffraction (XRD) images were recorded on a Ganesha lab instrument equipped with a Genix-Cu ultra-low divergence source producing X-ray photons with a wavelength of 1.54 Å and a flux of 1x108 photons/second. Diffraction patterns were collected on a Pilatus 300K detector with reversed-biased silicon diode array sensor. The detector consists out of three plates with a 17 pixels spacing in between, resulting in two dark bands on the image. Gracing Incidence X-Ray Scattering (GIXS) measurements were performed on a sample to detector distance of 1080 mm (WAXS). Azimuthal integration of the obtained diffraction patterns was performed by utilizing the SAXSGUI software.



Fig S1-1. GIWAXS patterns of spin coated thin films of normal BTA-C10 (a) and deuterated BTA-C10 (b) obtained at room temperature.



Fig S1-2. GIWAXS patterns of spin coated thin films of normal BTA-C18 (a) and deuterated BTA-C18 (b) obtained at room temperature.

In Figures S1-1 and S1-2, the small angle reflections on the equator related to 2D lattice show hexagonal Col_h packing of molecular columns with a preferably edge-on (planar) orientation, with some presence of face-on oriented domains. The broad diffusive halo is attributed to flexible alkyl side-chains rearrangements on the surface. Minor differences in the intensity of GIWAXS diffraction patterns in Figs. S1-1 and S1-2 can be attributed to minor thickness variations and possibly small differences in the degree of crystalization.

2 – Temperature dependence of P_r



Fig S2. Variation of the remnant polarization P_r of BTA-C10(h) and BTA-C18(h) with temperature.



Fig S3. Differential scanning calorimetry (DSC) traces of normal vs deuterated BTA-C10 (a) and BTA-C18 (b) obtained at the 2nd cycle.

4 – Amide deuteration procedure

BTA-C10 and BTA-C18 (1 g) were dissolved in 5 ml $CDCI_3$ in a 50 ml one necked round-bottom flask and 20 ml CD_3OD was then added into the flask. After stirring overnight in inert atmosphere, the solvent was removed in vacuo and the obtained deuterated product was obtained as a white solid.

As a result H/D exchange has been obtained for both BTA compounds:



Equivalent exchange:



Successful hydrogen/deuterium (H/D) exchange was detected via FT-IR and ¹H NMR spectroscopies, see next sections.

5 – IR showing complete deuteration

FTIR of BTA-C10, 18 and deuterated BTA-C10, 18:

FT-IR spectra were recorded at room temperature on a Perkin Elmer Spectrum One spectrometer equipped with a universal Attenuated Total Reflectance (ATR) sampling accessory. In the FTIR data, the stretching mode of the *N*-*H* bond is 3200-3300 cm⁻¹, after deuteration, the *N*-*D* equivalent is lowered to 2400 cm⁻¹ due to the greater mass of deuterium.



Fig. S5-1 Infrared (IR) Vibrational Spectroscopy on BTA-C10.



Fig. S5-2 Infrared (IR) Vibrational Spectroscopy on BTA-C18.

6 – NMR showing deuteration

¹H NMR of BTA-C10, BTA-C18 and deuterated BTA-C10, BTA-C18:

NMR spectra were recorded at room temperature in $CDCI_3$ solution on a Varian Gemini 400 MHz spectrometer (400 MHz for ¹H NMR, 100 MHz for ¹³C NMR). Proton chemical shifts are reported in ppm with respect to tetramethylsilane (Si(CH₃)₄, TMS, 0 ppm) Carbon chemical shifts are reported downfield from TMS using the resonance of $CDCI_3$ as the internal standard. The chemical shift of the proton in amide (*N*-*H*) is 6.62 ppm. After deuteration, the deuterium (*D*) chemical shift has disappeared from the ¹H NMR spectrum since the *D* signals are of different energy and are not seen at the ¹H NMR.

The slight shift of the signal from proton at the benzene ring (slightly above 8 ppm) at the Figs. S6-1(a) and S6-2(b) with respect to solvent $CHCl_3$ peak (7.23 ppm) might be due to the work up or the substitutions.



Fig. S6-1 Nuclear Magnetic Resonance (¹H NMR) on normal (a) vs deuterated BTA-C10 (b).



Fig. S6-2 Nuclear Magnetic Resonance (¹H NMR) on normal (a) vs deuterated BTA-C18 (b).

7 – Polarization retention measurements





Fig. S7-1 Remnant polarization *P* vs. delay time *t* between poling and probing signals (main panels) and current transients (insets) of regular BTA-C10 at different temperatures: 70 °C (a), 100 °C (b) and 120 °C (c). The remnant polarization varies slightly at different temperatures as the data have been measured on different devices. The slight change in current transient at 120 °C is attributed to slight molecular alignment distortions. Importantly, these do not affect the overall homeotropic alignment as witnessed by the constant remnant polarization value even at high temperatures and long depolarization times.





Fig. S7-2 Current transients of the polarization retention measurements of regular BTA-C10 (a) and deuterated BTA-C18 (b). The repolarization transients (first peak in the graph) have the same characteristics and shape as those corresponding to a normal polarization reversal.

8 – Scenario of depolarization by proton transfer



Fig. S8-1 Hypothetical depolarization mechanism by proton transfer. A new approaching proton results in tautomerization of the amide group of the molecule (H-N-C=O \rightarrow N=C-O-H). The further intermolecular proton transfer is accelerated by tunneling through hydrogen bonds. This process is followed by rotation of the N=C-O-H tautomeric form of the amide group. To complete the cycle, a second proton is picked up, transferred through the chain by the reverse process (N=C-O-H \rightarrow H-N-C=O) and a second amide rotation. That brings back the original situation, with two protons transferred along the chain. With time, the continuing process leads to a randomization of the macrodipole, i.e. polarization loss.