Electronic Supplementary Material (ESI) for ChemComm.

Supporting information for:

External Electric Field Reverses Helical Handedness of a Supramolecular Columnar Stack

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1 Solution phase

We have also explored the mechanism by which oligomers relax in bulk solution upon application of the applied field. The simulation was carried out by solvating an oligomer of size 20 in *n*-nonane solution at 298.15 K. An electric field of 0.01 V/Å was applied in a direction opposite to that of the macrodipole. Unlike the LC phase, the oligomer in solution is free to rotate. The stacks are seen to tumble over so as to align their macrodipole with $\vec{E}$, instead of the hydrogen bond reorganization that was observed in the LC phase. Such an overall rotation of the stack is not associated with change of handedness. The process is characterized by the angle between initial and instantaneous orientation of an oligomer as shown in Figure S1. The cosine of the angle starts at 1 and ends at around -1 indicating the antiparallel orientation of the final configuration with respect to the the initial one.

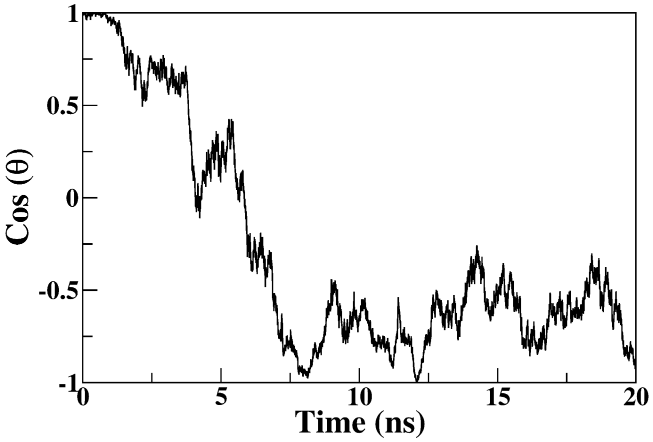


Figure S1: MD simulations of a pre-formed BTA oligomer of size 20 solvated in *n*-nonane solution. θ is the angle made by the long axes of the stack in its instantaneous configuration with respect to its initial configuration. The electric field is applied at t=0. In solution, the stack displays an overall rotation upon application of the electric field, with no change in handedness.

2 Additional computational details

Non-bonded interactions were truncated at 12 Å and long range Coulombic interactions were handled using particle-particle particle-mesh (PPPM) method. Long range corrections to energy and pressure were applied. Three-dimensional periodic boundary conditions were applied. In four of the simulations, α and β were fixed to 90° and the other four cell parameters $(a, b, c, and\ \gamma)$ were flexible. Full scaling for 1-4 interactions was adopted. The equations of motion were integrated with a time step of 0.5 fs.

Table S1: Mean value of the simulation cell parameters when field is in OFF state. Lengths and angles are in Å and degrees respectively.

System	No. of atoms	Run length	a	b	c	α	β	γ
2:1	10260	4 ns	58.2	57.8	35.4	90.0	90.0	113.6
3:0 (400 K)	10260	4 ns	60.9	60.3	35.0	90.0	90.0	58.7
3:0 (370 K)	10260	4 ns	60.1	58.5	35.0	90.0	90.0	61.7
racemic	12480	3 ns	44.3	91.6	35.1	96.6	97.2	77.9
chiral (9 decamers)	9720	4 ns	57.4	57.3	35.3	90.0	90.0	116.6
chiral (16 decamers)	17280	3 ns	55.8	100.1	35.0	81.7	87.1	74.6

Table S2: Mean value of the simulation cell parameters when field is in ON state. Lengths and angles are mentioned in Å and degrees respectively.

System	No. of atoms	Run length	a	b	c	α	β	γ
2:1	10260	5 ns	60.0	59.8	35.0	90.0	90.0	61.1
3:0 (400 K)	10260	2 ns	60.7	58.0	35.1	90.0	90.0	64.0
3:0 (370 K)	10260	5 ns	57.6	59.8	35.0	90.0	90.0	62.5
racemic	12480	3 ns	44.0	91.9	35.1	77.7	85.2	95.9
chiral (9 decamers)	9720	3.5 ns	58.0	56.9	35.1	90.0	90.0	115.8
chiral (16 decamers)	17280	3 ns	54.5	103.8	35.1	99.9	76.9	103.8

3 Liquid crystalline phase

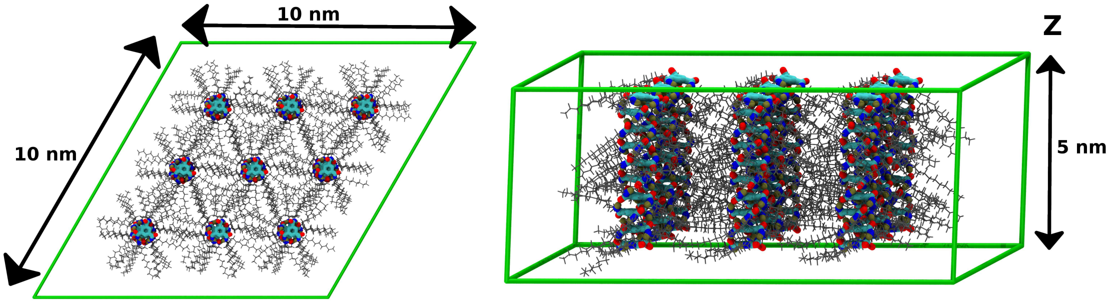


Figure S2: Top and side views of the initial configuration in the simulations of the LC phase whose final configuration is shown in Figure 2 of the main manuscript.

4 Determination of handedness of stack

The dihedral angle ($C_{Ar}-C_{Ar}-C-O$, see Figure S3) between the amide group and benzene plane determines the type of handedness taken by the hydrogen bonded helical network in an oligomer. The conditions on this angle can be described as follows:

$$Dihedral\ angle(\theta) = \begin{matrix} \left.\begin{matrix} -90^\circ < \theta < 0^\circ \\ 90^\circ < \theta < 180^\circ \end{matrix}\right\} Left-handed \\ \left.\begin{matrix} -180^\circ < \theta < -90^\circ \\ 0^\circ < \theta < 90^\circ \end{matrix}\right\} Right-handed \end{matrix} \tag{1}$$

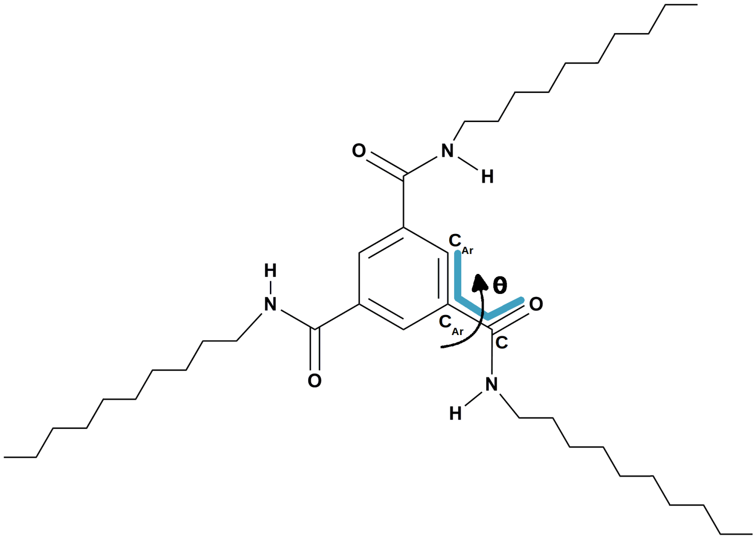


Figure S3: *N,N',N"*-tris(decyl)benzene-1,3,5-tricarboxamide. Value of the dihedral angle ($C_{Ar} - C_{Ar} - C - O$) determines the type of handedness of the hydrogen bonded helical network in an oligomer. One such dihedral is marked.

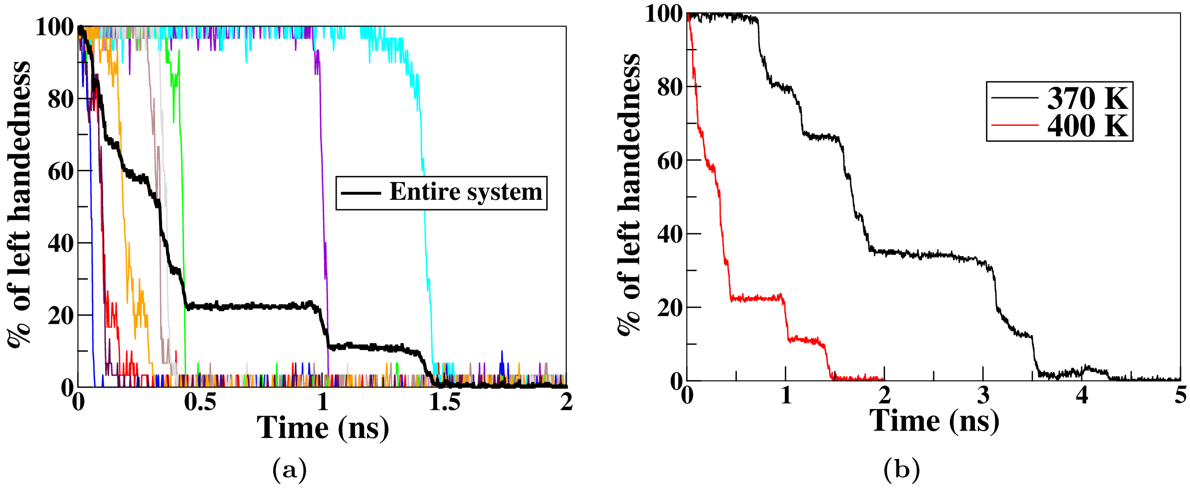


Figure S4: (a) Switching of handedness of each oligomer in the LC phase, upon application of an external electric field of magnitude 0.2 V/Å as a function of time. Each color indicates a different oligomer. Black is the average and is the same as the one shown in Figure 5 of main manuscript. (b) Comparison of the reversal of handedness at two different temperatures. Upon cooling the system, handedness reversal is slowed down.

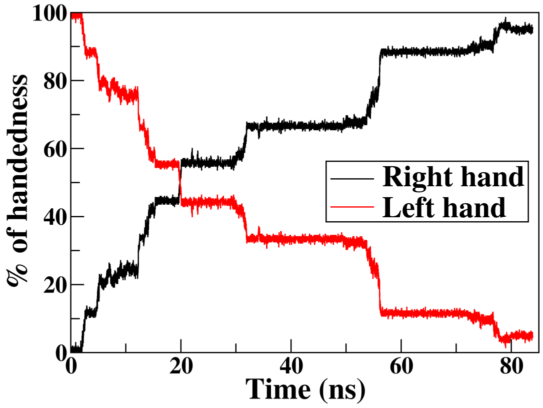


Figure S5: Progress of the transformation from left-handed to right-handed enantiomers by applying a small field of magnitude 0.1 V/Å (which is twenty five times that applied typically in experiments[S1]). The MD simulations were carried out at 400 K. Reversal of handedness is seen to be accompanied with defects (≈ 5%). Herein, the defect refers to a dihedral whose handedness does not change while the macrodipole aligns with the field. Experiments to observe handedness reversal may be performed at low temperatures so as to decrease the concentration of such defects.

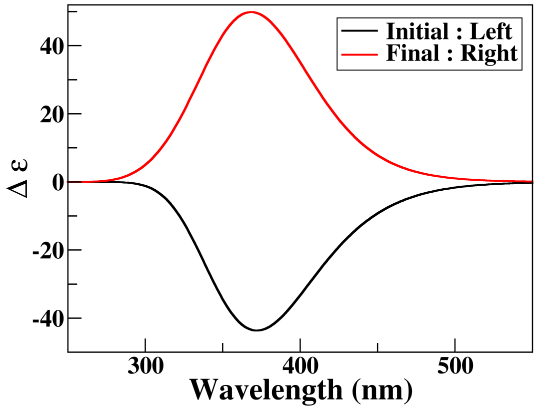
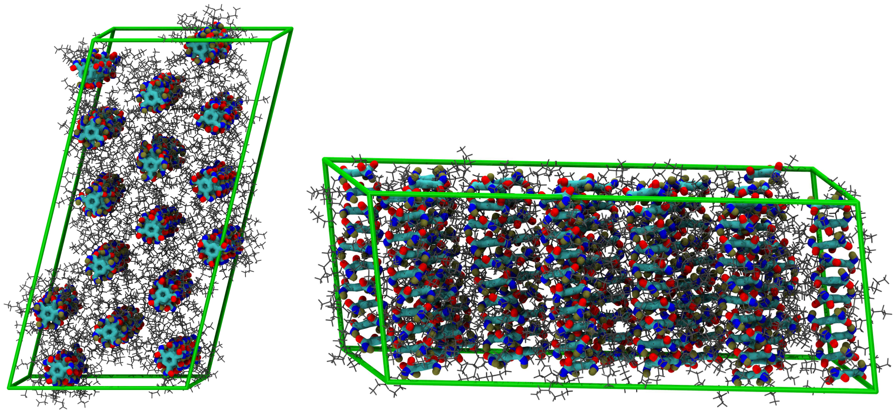


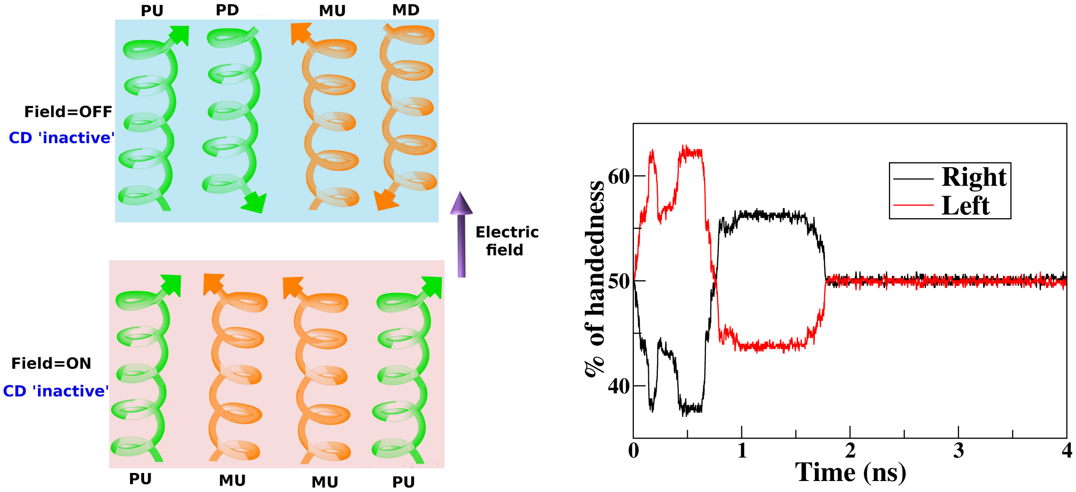
Figure S6: Initial and final (upon application of E-field) geometries of an oligomer in the LC phase as described in Figure 4 of main manuscript were used as inputs to calculate the CD spectra using the semi-empirical ZINDO/s method.

5 Racemic mixture



(a) (b)

Figure S7: Top and side views of the final configuration in the simulation of the LC phase of a racemic mixture. MD simulation was carried out in fully flexible simulation cell at 400 K.



(a) (b)

Figure S8: (a) Schematic representation of the effect of an external electric field applied on a racemic mixture of stacks. Arrows refer to the direction of the macrodipole vector. Although the electric field transforms the handedness of the stacks which are anti-aligned with it, the resultant configuration continues to be racemic and chiro-optically inactive. (b) Fraction of left or right handedness in hydrogen bonded helices as probed through the dihedral ($C_{Ar} - C_{Ar} - C - O$)) as defined in Equation 1. As the initial configuration is a racemic mixture, 50% of each kind is seen. The external electric field converts anti-aligned, right-handed helices to aligned, left-handed helices. It also converts anti-aligned left-handed helices to aligned right-handed ones. Thus, the phase is chiro-optically inactive both in the presence (and absence) of the electric field.

6 Handedness switching of a chiral system aligned with the field

The LC phase of *N*-*((*S*)*-3,7-dimethyloctyl)-*N',N"*-di(7-methyloctyl)benzene-1,3,5-tricarboxamide was prepared in a fashion similar to that described for the LC phase of the achiral system. We considered that the macrodipole vectors of all the stacks are pointing along the same direction. We examine the case of a chiral system where the macrodipoles of stacks can be pointing either parallel or anti-parallel to the field in the main manuscript. In the present instant, the chiral (S)-center was present on one of the octyl tails (Figure S9). Post equilibration (duration of 2 ns), MD simulation with an electric field of 0.2 V/Å in a direction opposite to the direction of the macrodipole was applied. Within 8 ns, right-handed stacks switch their handedness so as to align with the field, similar to the phenomenon observed for achiral molecules.

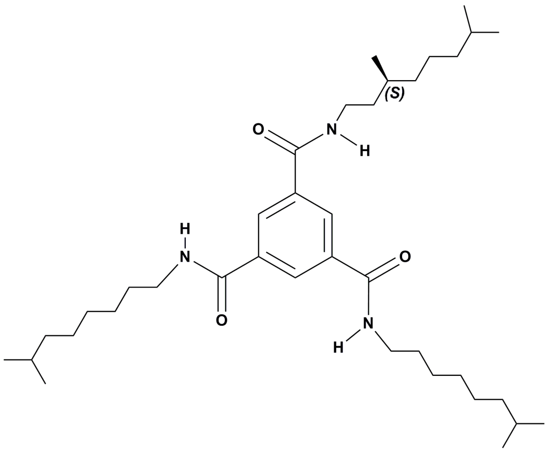


Figure S9: *N*-*((*S*)*-3,7-dimethyloctyl)-*N',N"*-di(7-methyloctyl)benzene-1,3,5-tricarboxamide

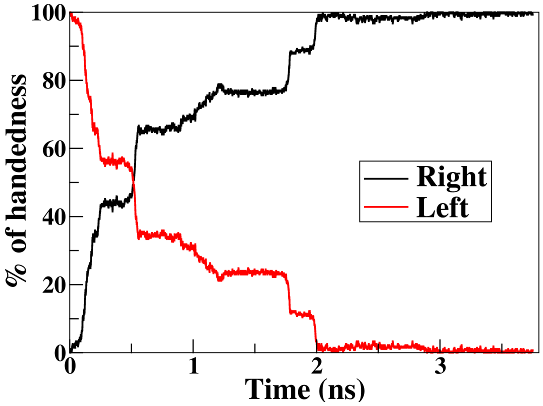


Figure S10: Progress in the reversal of handedness of a LC phase formed by chiral molecules. The molecule employed in the simulation is shown in Figure S9. Magnitude of the field is 0.2 V/Å and temperature is 400 K.

References

(S1) Fitié, C. F. C.; Roelofs, W. S. C.; Magusin, P. C. M. M.; Wübbenhorst, M.; Kemerink, M.; Sijbesma, R. P. Polar Switching in Trialkylbenzene-1,3,5-tricarboxamides. *J. Phys. Chem. B* **2012**, *116*, 3928–3937.