Electronic Supplementary Information

Theoretical Investigations of the 2D Chiral Segregation Induced by External Directional Fields

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1. Simulation details

The simulation algorithm was organized as follows. In the first step N molecules of a selected type (S, R) were distributed randomly on the lattice. Next, the adsorbed layer was equilibrated by a series of attempts to move each molecule to a new position (n). To that end the selected molecule was randomly translated and the four allowed orientations from Fig. 1 were probed. For each of these trial configurations, l the corresponding potential energy was calculated using the simple summation

$$E_{nl} = \omega \sum_{i=1}^{4} \sum_{j=1}^{4} s_{ij} - mB\cos(\theta_l) \qquad \text{for} \qquad l = 1..4 \qquad (1)$$

where the first sum runs over all segments of the selected molecule and the second sum runs over nearest neighbors of the segment i on a square lattice. The occupation variable s_{ij} is equal to 1 if the sites i and j are occupied by segments belonging to a pair of neighboring molecules. Otherwise it is equal to zero. In the next step of the simulation the associated Rosenbluth factor:

$$w_n = \sum_{l=1}^{4} \exp[-\beta E_{nl}] \tag{2}$$

was determined for the new position and one of the trial configurations, say *x*, was chosen with probability equal to

$$p_{nx} = \exp[-\beta E_{nx}] / w_n \tag{3}$$

where $\beta = 1/kT$ and *k* and *T* have their usual meanings. The same procedure (see Eqs. 2 and 3) was used to calculate the Rosenbluth factor for the old position, w_o including the original configuration of the selected molecule. To accept or reject the new configuration *x* the transition probability was calculated:

$$P = \min[1, w_n / w_o] \tag{4}$$

and it was compared with a randomly generated number $r \in (0,1)$. If $r < P$ the move was accepted; otherwise the molecule was left in the original configuration. All of the results described here were obtained for $\omega = -1$ and $m = 1$, assuming that *m*, *B*, ω, *k* and *T* are dimensionless parameters. To equilibrate the systems at a given value of *B* we used 2×10^7 MC steps per molecule, where one MC steps is a single attempt to move (and rotate) a molecule to a new position on the lattice. The same set of parameters was used to simulate the

overlayers comprising five-membered prochiral molecules discussed in the following section.

The results of this study are averages over ten independent systems replicas.

2. Snapshots of the enantiopure overlayers comprising five-membered molecules

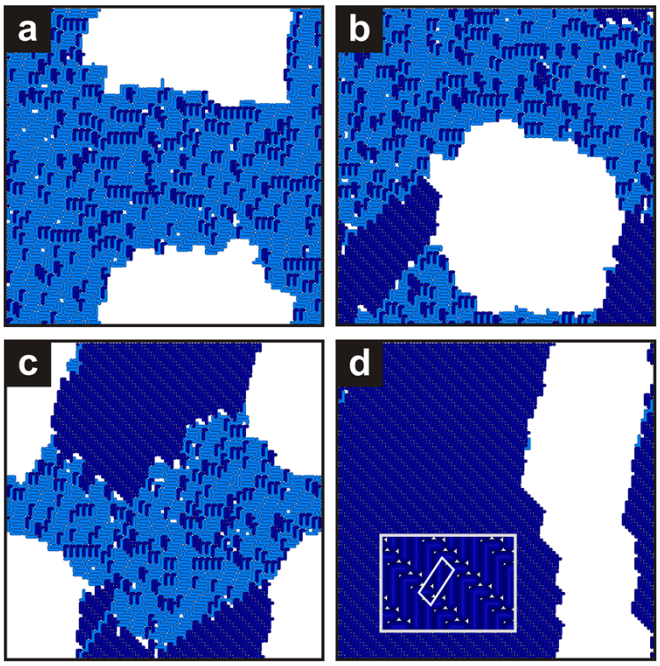

Figure S1. Snapshots of the enantiopure overlayer comprising 1400 molecules **1**(S) simulated for different strengths of the external field, B: a) 0.00, b) 0.36 c) 0.37 and d) 0.40; $T = 0.5$. The inset in panel d) presents a magnified fragment of the overlayer in which the parallelogram $(\sqrt{2} \times \sqrt{13})$ unit cell is marked in white. The molecules with upward orientation are colored in dark blue.

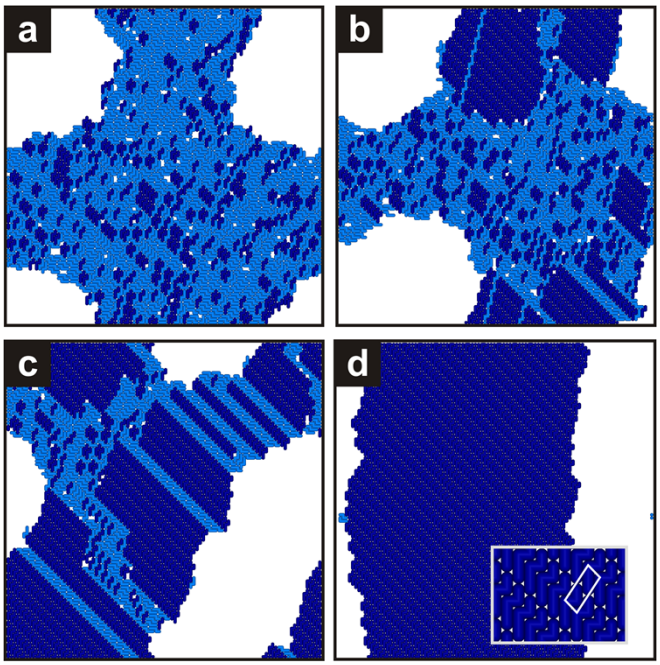

Figure S2. Snapshots of the enantiopure overlayer comprising 1400 molecules **2**(S) simulated for different strengths of the external field, B: a) 0.00, b) 0.21 c) 0.25 and d) 0.30; $T = 0.5$. The inset in panel d) presents a magnified fragment of the overlayer in which the parallelogram $(\sqrt{2} \times \sqrt{13})$ unit cell is marked in white. The molecules with upward orientation are colored in dark blue.

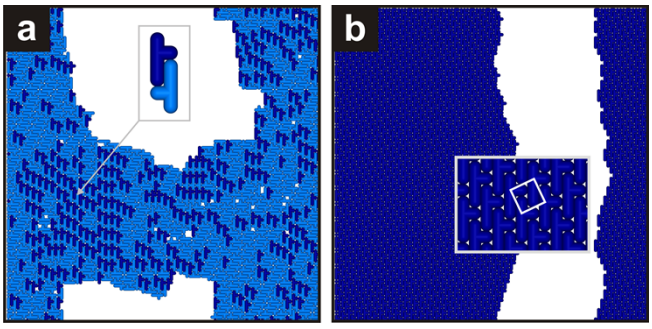

Figure S3. Snapshots of the enantiopure overlayer comprising 1400 molecules **3**(S) simulated for different strengths of the external field, B: a) 0.41 and b) 1.50; $T = 0.5$. The inset in panel a) shows the bimolecular configuration responsible for the stabilization of molecules with downward orientation (light blue). The inset in panel b) is a magnified fragment of the overlayer in which the square $(\sqrt{5} \times \sqrt{5})$ unit cell is marked in white. The molecules with upward orientation are colored in dark blue.

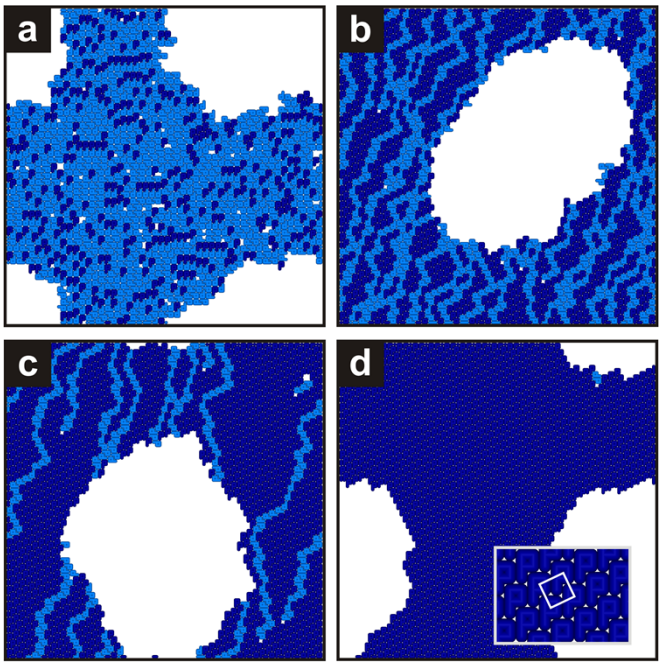

Figure S4. Snapshots of the enantiopure overlayer comprising 1400 molecules **4**(S) simulated for different strengths of the external field, B: a) 0.10, b) 0.32 c) 0.43 and d) 0.58; $T = 0.5$. The inset in panel d) presents a magnified fragment of the overlayer in which the square $(\sqrt{5} \times \sqrt{5})$ unit cell is marked in white. The molecules with upward orientation are colored in dark blue.

. **2. Snapshots of the racemic overlayers comprising five-membered molecules**

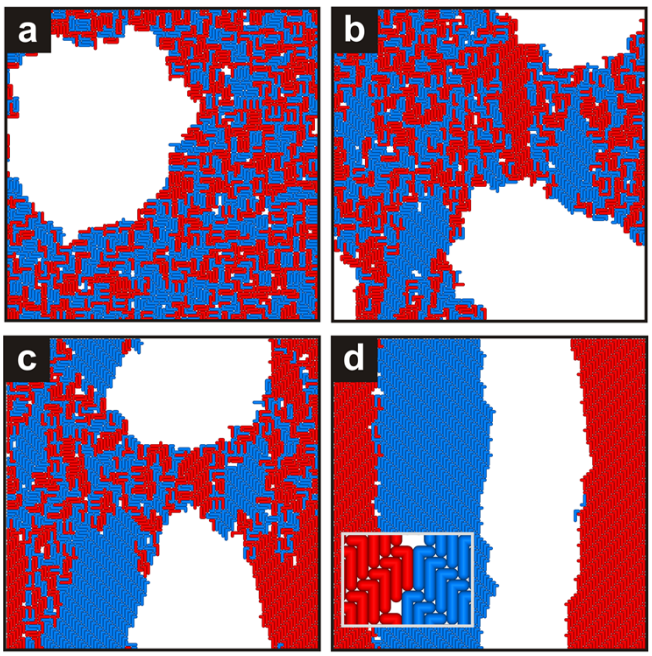

Figure S5. Snapshots of the racemic overlayer comprising 700 S + 700 R molecules **1** simulated for different strengths of the external field, B: a) 0.10, b) 0.36 c) 0.37 and d) 0.40; $T = 0.5$. The inset in panel d) presents a magnified fragment of the overlayer.

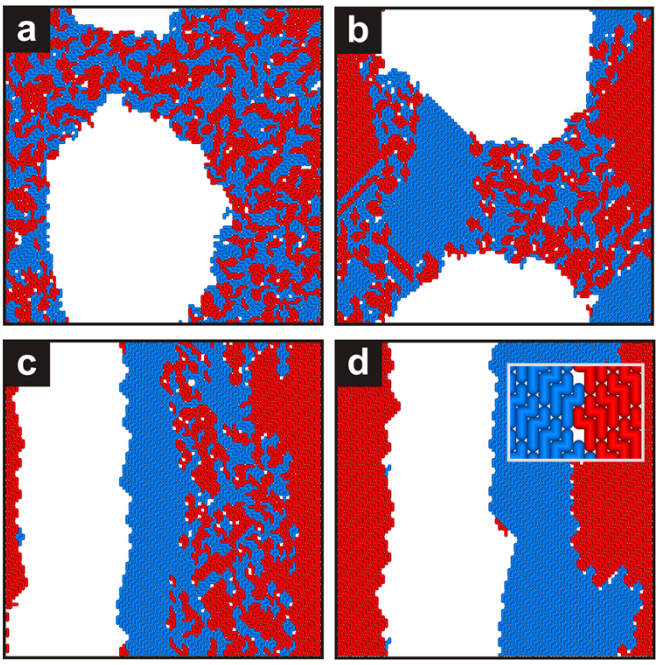

Figure S6. Snapshots of the racemic overlayer comprising 700 S + 700 R molecules **2** simulated for different strengths of the external field, B: a) 0.10, b) 0.60 c) 0.66 and d) 0.80; $T = 0.5$. The inset in panel d) presents a magnified fragment of the overlayer.

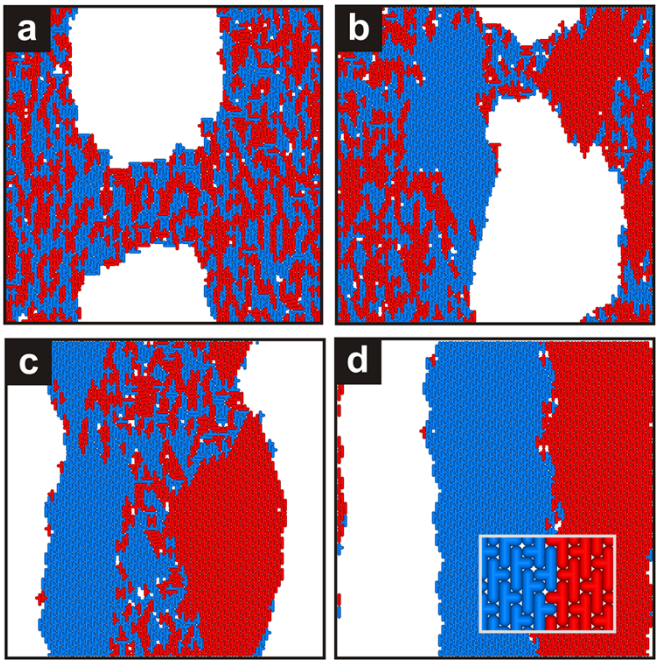

Figure S7. Snapshots of the racemic overlayer comprising 700 S + 700 R molecules **3** simulated for different strengths of the external field, B: a) 0.20, b) 0.51 c) 0.55 and d) 0.74. The inset in panel d) presents a magnified fragment of the overlayer.

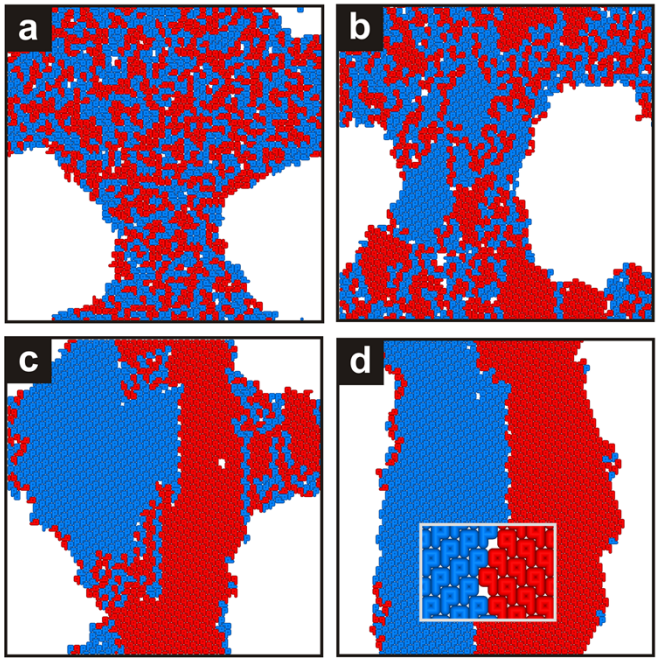

Figure S8. Snapshots of the racemic overlayer comprising 700 S + 700 R molecules **4** simulated for different strengths of the external field, B: a) 0.2, b) 0.87 c) 0.90 and d) 1.00; $T = 0.5$. The inset in panel d) presents a magnified fragment of the overlayer.

3. Statistics of molecules with different orientations

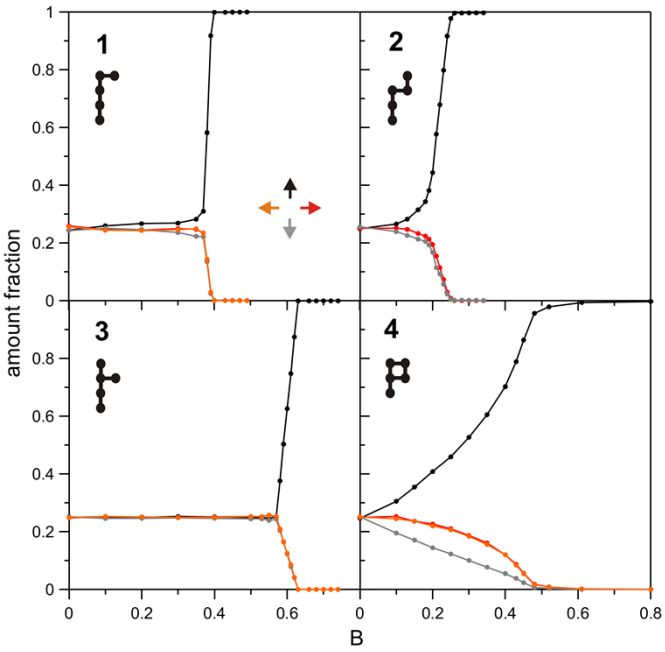

Figure S9. Effect of the external field on the amount fraction of molecules **1-4** with the orientations indicted by the colored arrows from panel 1; enantiopure overlayers, 1400 S; $T = 0.5$.

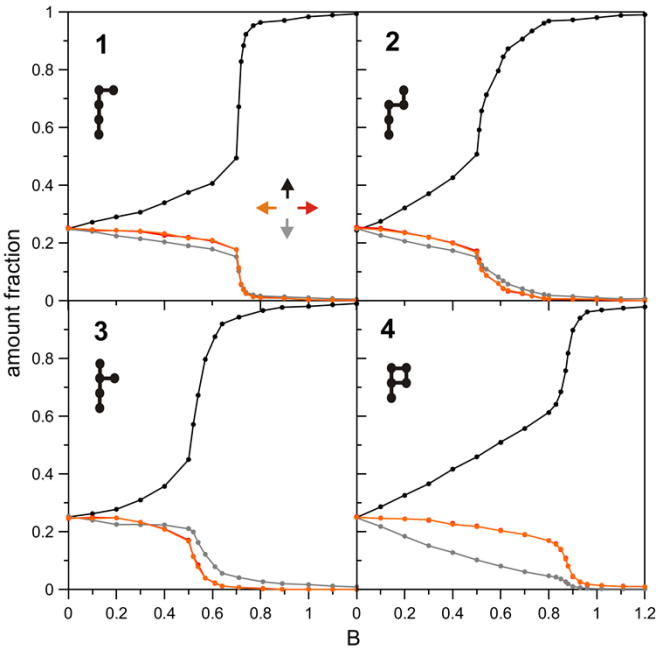

Figure S10. Effect of the external field on the amount fraction of molecules **1-4** with the orientations indicted by the colored arrows from panel 1; racemic mixtures, 700R + 700S; $T = 0.5$.