Supporting information

**Role of molecular orientational anisotropy in the chiral resolution of enantiomers in adsorbed overlayers**

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**Figure S1.** Snapshots of the racemic overlayer comprising 900 R + 900 S molecules of **A** obtained during the relaxation process at $T=0.5$. The relaxation procedure started with the overlayer in which a complete segregation induced by the orientational symmetry breaking was achieved (first panel). In subsequent simulation steps the adsorbed molecules were allowed to take the four orientations assumed in the isotropic model. The snapshots were taken after $n_{MC} \times 10^3$ MC steps and n_{MC} is indicated in each panel.
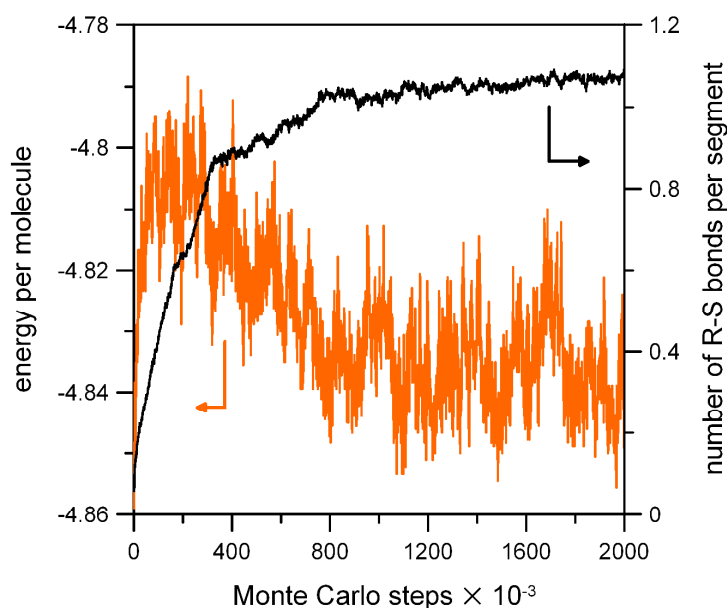
Figure S2. Changes in the potential energy (orange) and number of R-S bonds (black) during the relaxation of the racemic overlayer from Fig. S1 (900 R + 900 S molecules of **A** at $T = 0.5$).
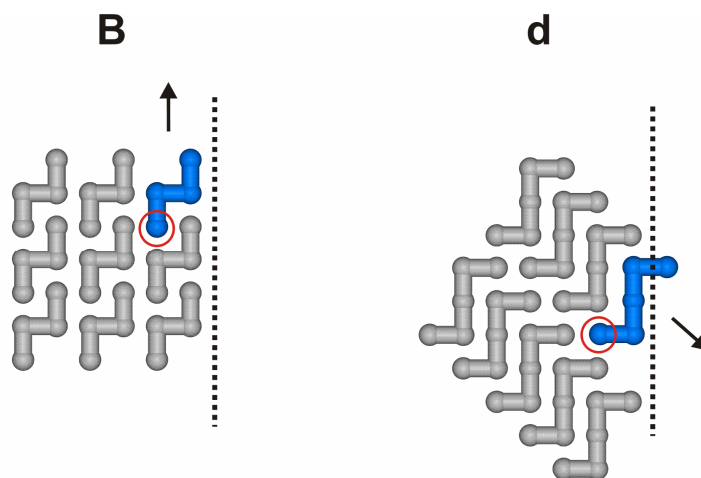

Figure S3. Differences in the formation of enantiopure domain walls by molecules of **B** and **d** in the directional model. Both molecules tend to occupy empty peripheral sites in such a way that each molecular segment achieves the highest accessible coordination number. Of a special importance are the three-fold sites marked by red circles, as these sites are characterized by the lowest potential energy. The position of the lowest-energy sites directs the incorporation of a new molecule (blue) into the growing enantiopure cluster (grey). For a molecule of **B** this effect is responsible for the vertical alignment of the molecules (black arrow on the left). In the case of **d**, the formation of vertical walls is highly unfavorable from an energetic point of view. Namely, if the vertical wall was formed (see dashed lines), there would be a large number of unoccupied three-fold sites left in the structure. For that reason vertical phase boundaries are not created by molecules of **d**, and instead the attachment of a molecule of **d** leads to the creation of walls running along diagonal directions (black arrow on the right).
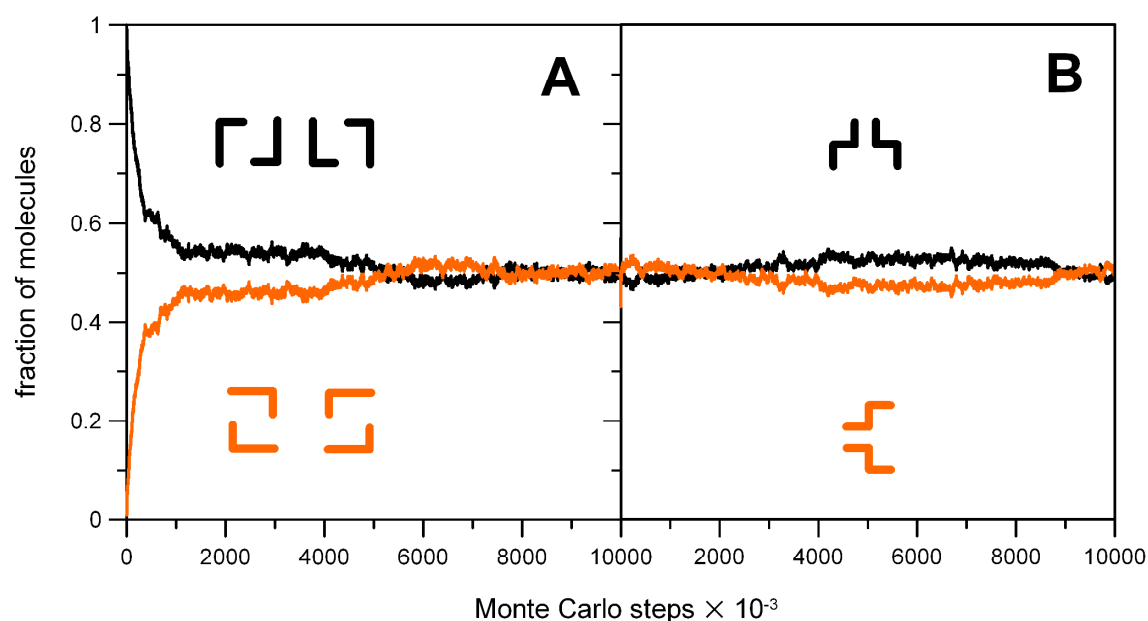
Figure S4. Fraction of molecules having vertical (black) and horizontal (orange) orientation obtained for the racemic overlayers comprising 900 R + 900 S molecules of **A** (left) and **B** (right) at $T = 0.5$. The insets show those molecular orientations which we considered vertical and horizontal. The results shown for the molecule **A** correspond to the relaxation process whose first 2000×10^3 MC steps are illustrated in Fig. S1 and S2. The curves from the right part were calculated starting from a random distribution of molecules of **B**. The final structure obtained for the molecule **B** after 10^7 MC steps is that one shown in Fig. 3.
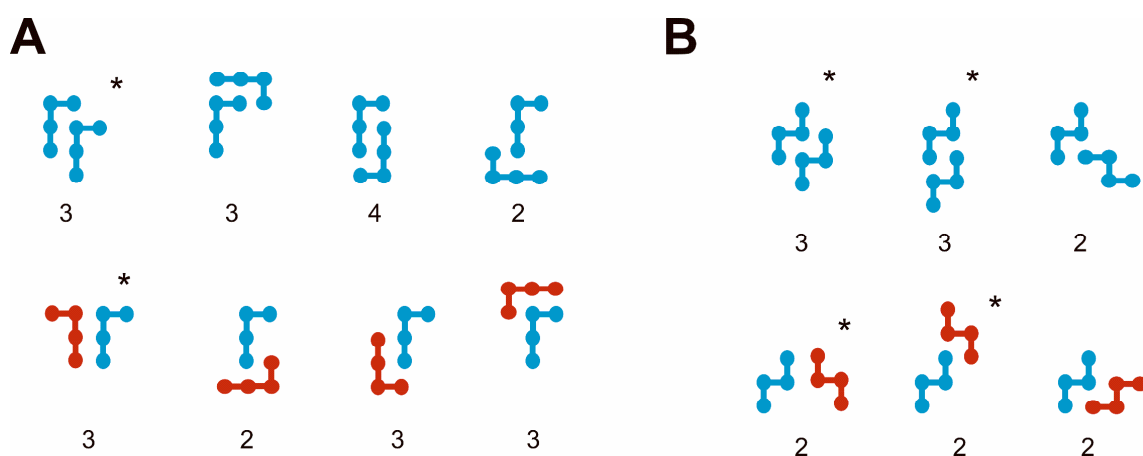
Figure S5. Examples of the possible adsorbed configurations of adjacent four-membered molecules used in the simulations. The figure presents examples of those configurations which are characterized by the lowest molecule-molecule interaction energy at given relative orientation of the enantiomers. The energy of interaction, expressed in ω units, is given below each structure. The configurations marked with an asterisk correspond to the unidirectional model.
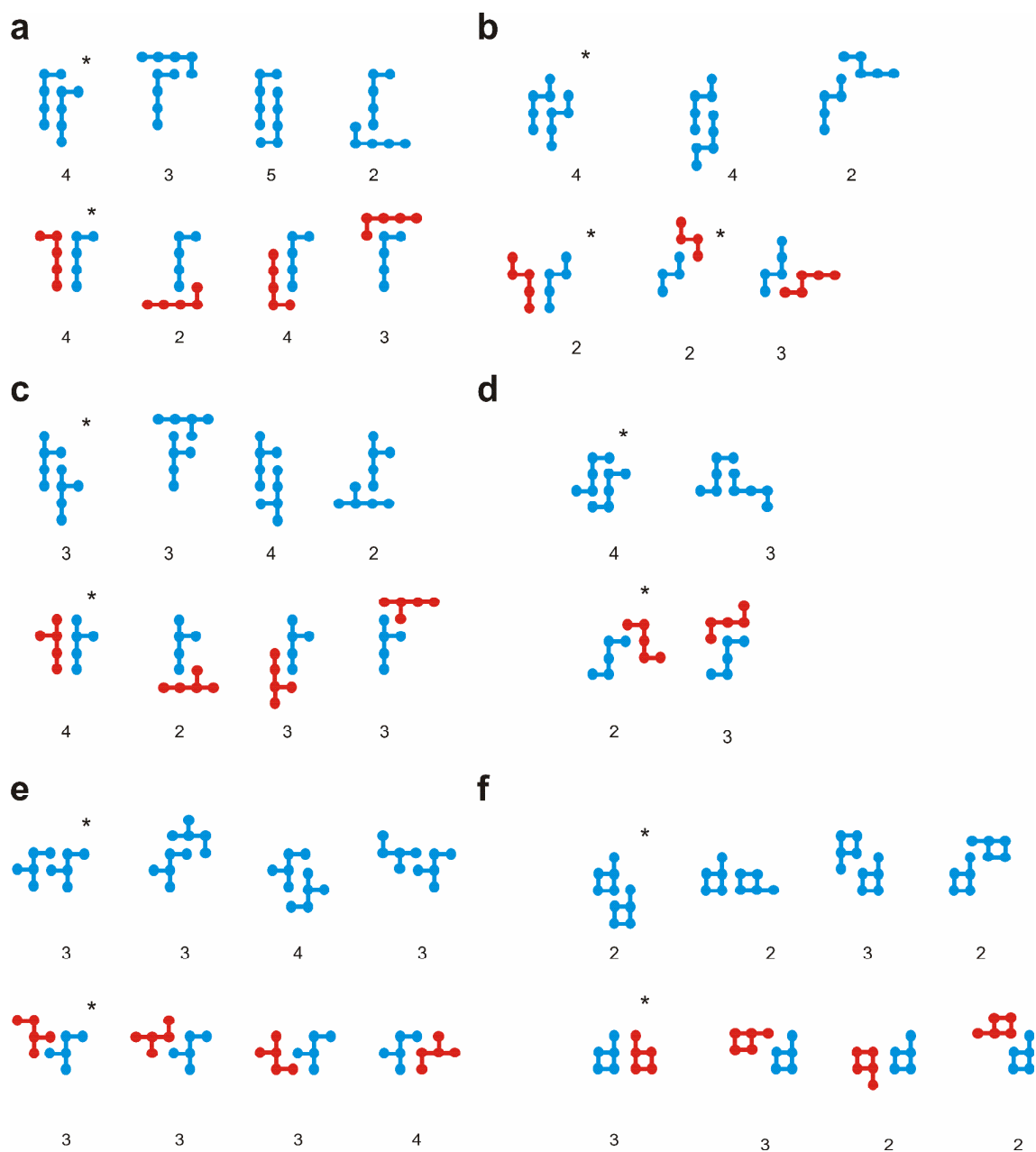
Figure S6. Examples of the possible adsorbed configurations of adjacent five-membered molecules used in the simulations. The figure presents examples of those configurations which are characterized by the lowest molecule-molecule interaction energy at given relative orientation of the enantiomers. The energy of interaction, expressed in ω units, is given below each structure. The configurations marked with an asterisk correspond to the unidirectional model.