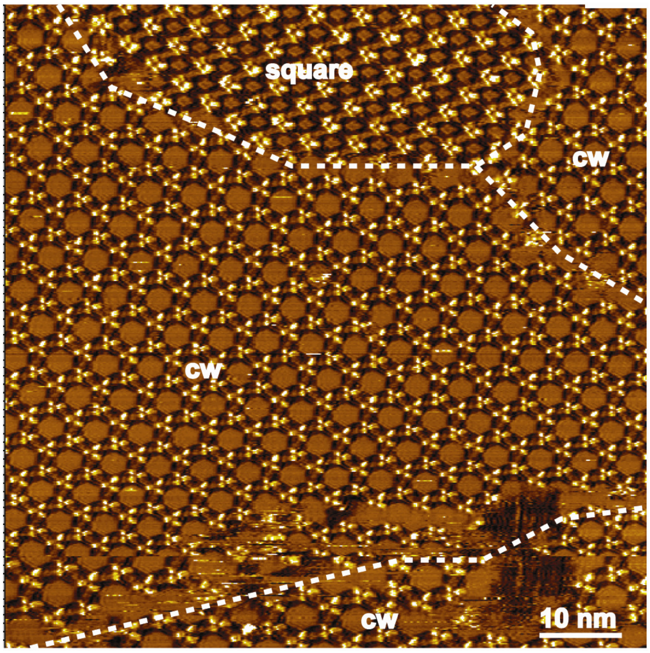
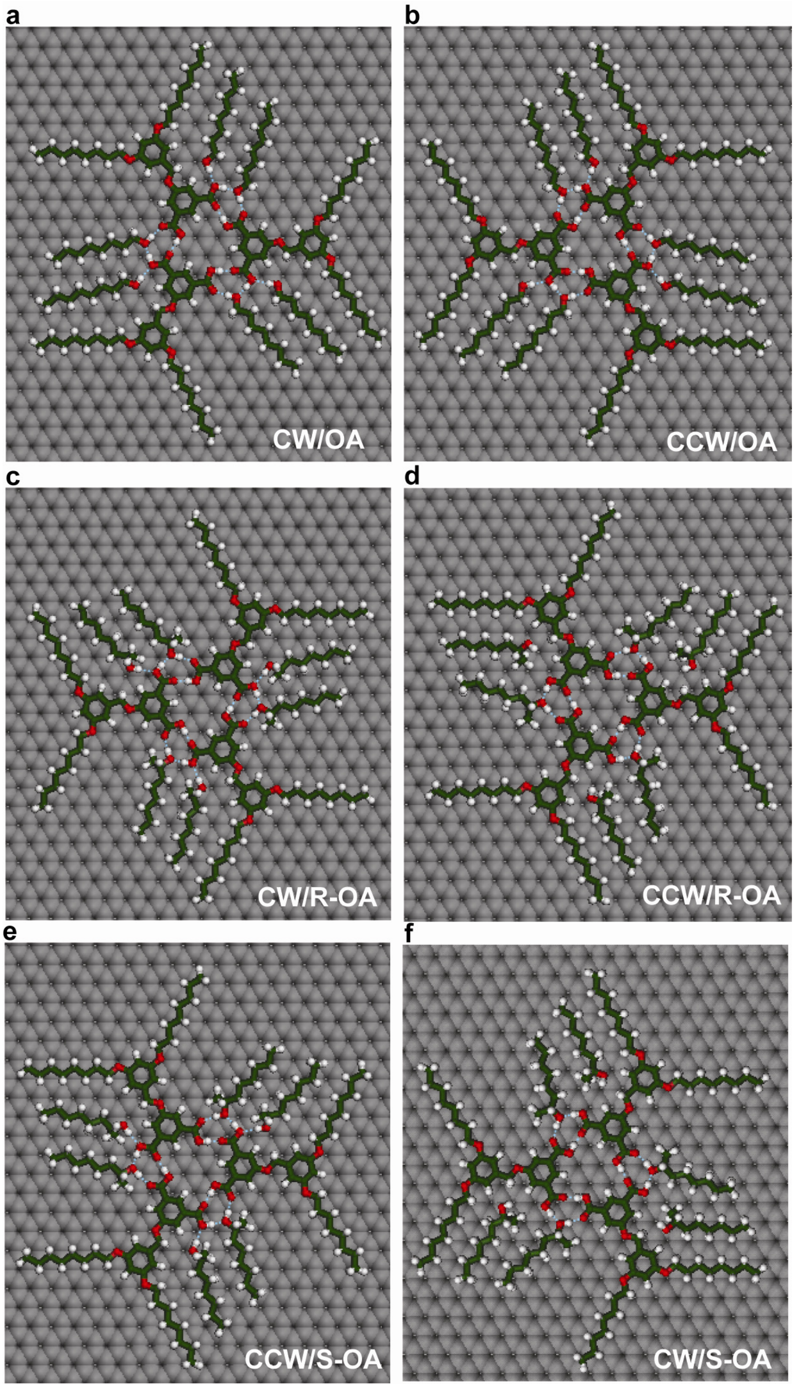
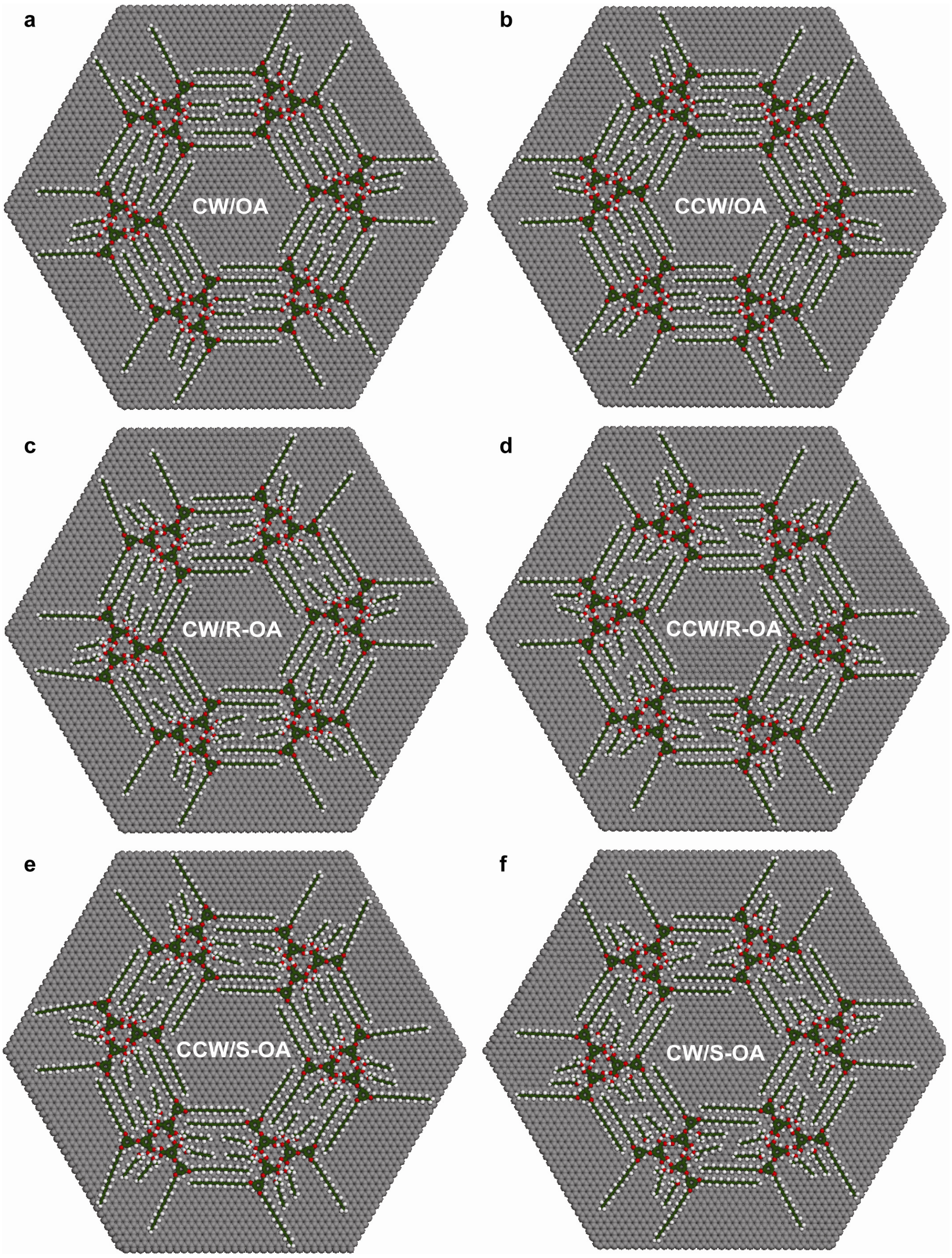


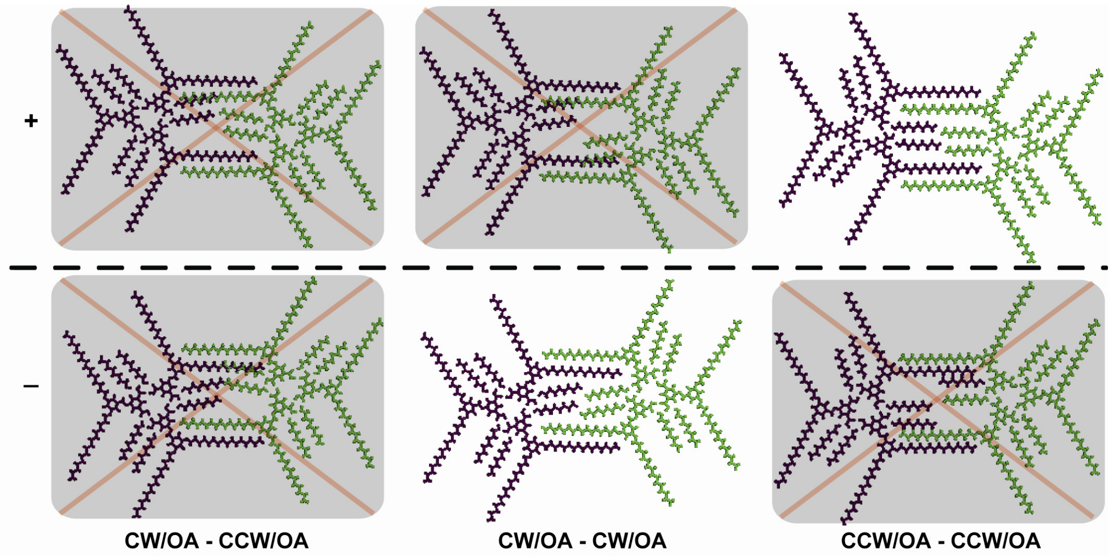
Supplementary Figure S1 BIC assembly in diluted chiral 2-octanol. STM image (93 × 93 nm^2, $I = 0.180$ nA, $V_{\mathrm{bias}} = 0.860$ V) of BIC assembly at the presence of R-OA (10%) and OB. The dotted lines indicate the domain boundarites. CW and square represent the domain possess CW network and square structure, respecitively.



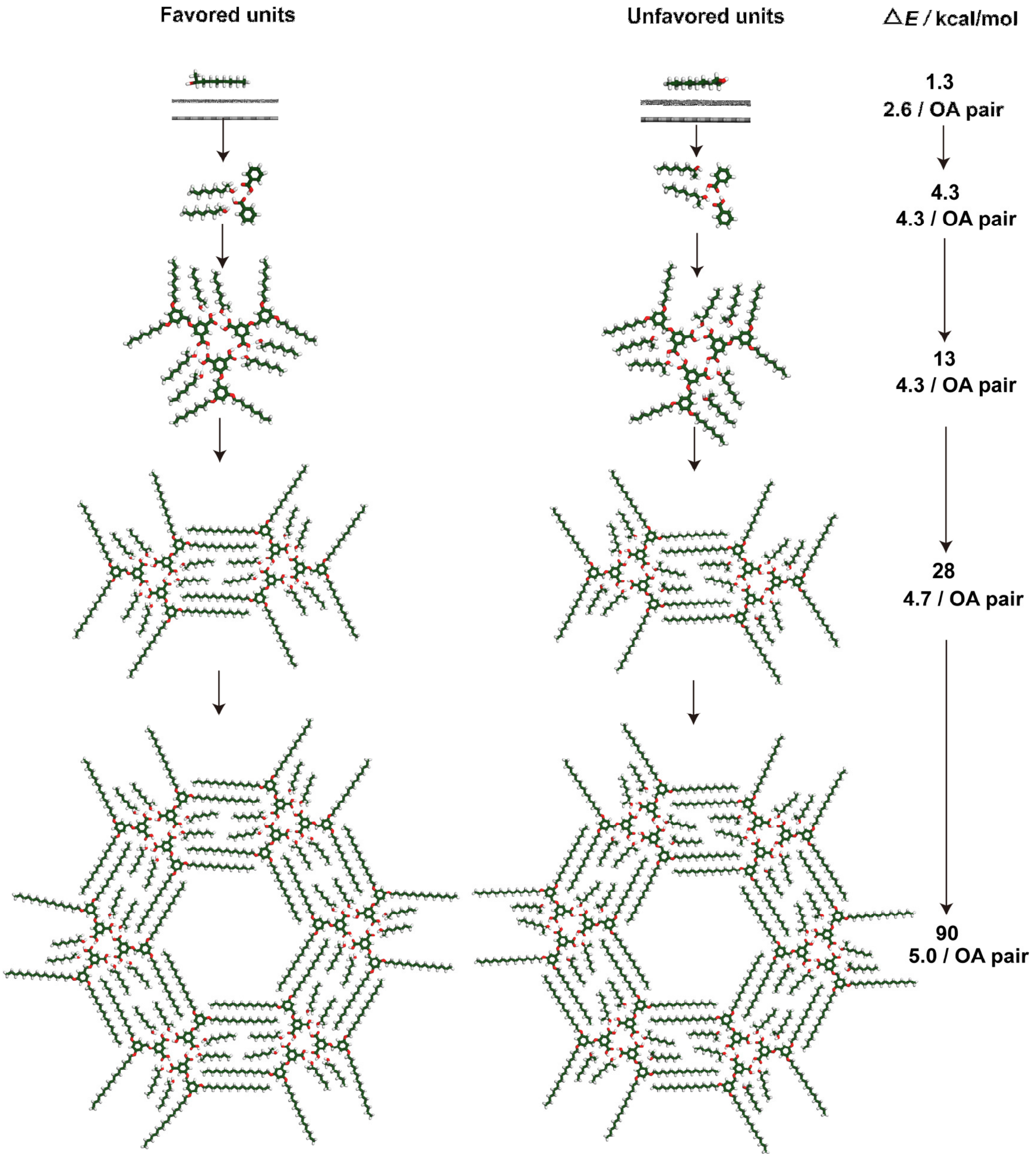
Supplementary Figure S2 Optimized structures from MM simulations of the triangular units. a, CW/OA unit. b, CCW/OA unit. c, CW/R-OA unit. d, CCW/R-OA unit. e, CCW/S-OA unit. f, CW/S-OA unit. The hexadecyloxy chains in BIC are replaced by octyloxy groups for simplicity.



Supplementary Figure S3 Optimized structures from MM simulations of the hexagonal units. a, CW/OA unit. b, CCW/OA unit. c, CW/R-OA unit. d, CCW/R-OA unit. e, CCW/S-OA unit. f, CW/S-OA unit.



Supplementary Figure S4 Possible interdigitation modes of the consecutive trimer units at the OA/HOPG interface. The trimer units are colored for distinguishable. The red crosses represent the structures are unfavored.



Supplementary Figure S5 Schematic illustration of the induction and the hierarchical amplification of homochirality. Favored Units are R-OA conformer with methyl group pointing away from the substrate and its combinations with the CW enatiomers of BIC aggregations as an example. These units can be observed in STM images and revealed to be energetically favored by MM simulations. Unfavored units are R-OA conformers with methyl group pointing to or paralleling to the surface and its combinations with the CCW enantiomers of BIC aggregations. Actually these units do not exist in the BIC assembly and are proposed according to the favored units for comporison. All the units shown here are optimized structures by MM simulations. Δ*E* refers to the total energy difference between the favored units and their corresponding unfavored units. Namely, $\Delta E = E_{\mathrm{unfavored}} - E_{\mathrm{favored}}$.

Supplementary Table S1. The population of the different assemlies in monolayer for diluted majority rules experiments.[*]

ee of S-OA (%)	C_{OA} (%)	Composition of the assembly		
		R_{CW} (%)	R_{CCW} (%)	R_{sq} (%)
-5.2[**]	50	100	—	—
	20	100	—	—
	16	100	—	—
	10	71 ± 11	—	29 ± 11
	5.0	—	—	100
-2.6	96	100	—	—
	80	93 ± 1.2	7.0 ± 1.2	—
	50	62 ± 6.8	38 ± 6.8	—
	20	57 ± 8.9	43 ± 8.9	—

"—" represents the structure is not observed.

[*] Excess of S-OA is defined as ee = $(N_S - N_R)/(N_S + N_R)$, where N_S and N_R are the amount of S-OA, R-OA in the mixed solution, respectively. Fraction of 2-octanol in the solution is calculated according to $C_{OA} = (N_S + N_R)/(N_S + N_R + N_{OB})$, where N_S, N_R, and N_{OB} are the amount of S-OA, R-OA, and OB in the mixed solution respectively. To calculate the percentage of CW network, CCW network, and square structute in the assembly, 3 samples were prepared for each measurment and 20 STM images with scan area of 100 × 100 nm^2 were recorded at different locations for each sample. The area of the CW network, CCW network, and square structure in the STM images for one sample were summed up together, denoted with A_{CW}, A_{CCW}, and A_{sq}, respectively. The area percentages of different structures is calculated according to $R_{CW} = A_{CW}/(A_{CCW} + A_{CW} + A_{sq})$, and $R_{CCW} = A_{CCW}/(A_{CCW} + A_{CW} + A_{sq})$, and $R_{sq} = A_{sq}/(A_{CCW} + A_{CW} + A_{sq})$. The area percentage giving in the paper is an average value of 3 samples.

[**] Results obtained at ee = 50.0 and 11.1 are similar to the results at ee = 5.2. When C_{OA} is higher than 16.0%, all the assembly are CW networks. At C_{OA} = 10.0%, the assembly are consisted of CW networks and square structures. When the C_{OA} decreases to 5.0, all the domains analyzed show square structures.

Supplementary Methods

Rough derivation of the entropy in the majority rules For an ideal mixed solution, which is generally true for the mixture of enantiomers, the entropy of mixing is

$$\Delta S = -nR(x_1 1 \ln x_1 + x_2 \ln x_2)$$

where R is the gas constant, n is the total number of molecules, and x_1, x_2 are the mole fractions of component 1 and 2, respectively, and $x_1 + x_2 = 1$.

After simple mathematic analysis, we know that ΔS achieve maximum when

$$\frac{d\Delta S}{dx_1} = 1 + \ln x_1 - [1 + \ln(1 - x_1)] = 0$$

namely, $x_1 = x_2 = 0.5$.

That means, the entropy of the solution phase reaches maximum when the percent of two component are equal.

Therefore, when the solution contains two components in unequal fraction, the majority rather than the minority in the solution tends to adsorb on solid surface to help increasing the entropy of the solution phase during the nucleation process.

Molecular mechanics simulations

MM simulations provide quantitative description of energy landscape during the induction and hierarchical amplification of homochirality, as shown in Supplementary Fig. S5. The energy for the δ-OA and γ-OA conformers is the same. Their relative total energy remains equivalent when δ-OA and γ-OA conformers bind with one chiral pocket in the CW and CCW BIC trimers, respectively. Thus, both CW/OA and CCW/OA enantiomeric trimer units co-exist in the BIC assembly. With the introduction of the chiral carbon, two possible adsorption conformations exist for R-OA or S-OA molecule: conformers with the methyl groups pointing away from or paralleling to the substrate, named α- and β-conformer, respectively (The conformer with methyl group pointing to the substrate is converged to β-conformer after geometry optimization.) MM simulations suggest that the α-conformer is energetically favored with relative adsorption energy of 1.3 kcal/mol, i.e. 2.6 kcal/mol/OA pair. The hydroxyl group of α-R-OA fit exactly to the hydrogen-bonding pocket in the CW BIC trimer, whereas β-conformer of R-OA is required to fulfill the hydrogen bonding formation with the pocket in the CCW BIC trimer. Therefore, although CW and CCW trimers have equal formation energy, the specific recognition between hydrogen-bond pocket and guest molecules has transferred the energy bias for the formation of two conformers of R-OA to the formation of CW enantiomeric trimer of BIC. As revealed by MM simulations, the relative total energy difference between α-R-OA/CW pocket structure and β-R-OA/CCW pocket structure has been further amplified to about 4.3 kcal/mol/OA pair. The intermolecular interactions, including hydrogen bonding between R-OA and the chiral pocket and van der Waals interactions between the alkyl chains, are supposed to account for the larger energy difference. Finally, the energy bias for R-OA/CW trimer is further amplified during the interdigitated arrangement of trimers to form hexagonal units due to difference in the intermolecular van der Waals interactions. The total energy for a α-R-OA/CW hexagonal unit, which is consisted of six consecutive α-R-OA /CW trimer units, is 90 kcal/mol, or 5 kcal/mol/OA pair, lower than that of a β-R-OA /CCW hexagonal unit. The hierarchical nature of BIC assembly strengthens the bias of one special α-conformer of R-OA from 2.6 kcal/mol/OA pair to 5.0 kcal/mol/OA pair and accounts for the 100% ee of one of two enantiomorphous networks in the presence of chiral co-absorbers.