Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information

Transfer of chiral information from a chiral solvent to a two-dimensional network

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1. Materials and Methods

STM measurements:

The STM experiments were performed at room temperature (20–25°C), except for the temperature treatment experiments, using a PicoLE (Agilent) or PicoSPM (Molecular imaging, now Agilent) machine operating in constant–current mode with the tip immersed in the supernatant liquid. For the temperature treated experiments, the samples were placed on top of a heating stage that was controlled via a feedback loop using a Lakeshore model 331 temperature controller. This arrangement provides an accessible temperature range from room temperature up to ~80°C. STM tips were prepared by mechanical cutting from Pt/Ir wire (80%/20%, diameter 0.2 mm). The DBAs were synthesized according to published protocols.[1] The solvents (*S*)-2-heptanol (Sigma-Aldrich 98%), (*S*)-2-octanol (Alfa Aesar 99%), (*R*)-2-octanol (Alfa Aesar 99%), (*S*)-2-nonanol (Sigma-Aldrich 97%) (*R*)-2-decanol (Sigma-Aldrich 97%) and (*rac*)-2-octanol (Sigma-Aldrich 99.5%) were used without further purification. (*S*)-2-hexanol (Sigma-Aldrich 98%) was distilled before use. (*S*)-2-dodecanol was synthesized in house according to ref. 2. DBA derivatives were dissolved in these solvents by gentle heating at 60-65°C. The concentrations used in the experiments ranges from 1.4×10^{-6} - 4.2×10^{-6} molar. Prior to imaging, a drop of the solution was applied onto a freshly cleaved surface of highly oriented pyrolytic graphite (HOPG, grade ZYB, Advanced Ceramics Inc., Cleveland, USA or HOPG, grade ZYB, Optigraph GMBH, Berlin, Germany). The experiments were repeated in several sessions using different tips to check for reproducibility and to avoid experimental artifacts, if any. For analysis purposes, recording of a monolayer image was followed by consecutive imaging the graphite substrate underneath. This was done under the same experimental conditions but by lowering the substrate bias (typically V_{bias} = 1 mV) and increasing the tunneling current (typical I_{set} = 1000 pA.) From the atomically resolved STM image of HOPG one can easily obtain the graphite symmetry axes. The images were corrected for drift via Scanning Probe Image Processor (SPIP) software (Image Metrology ApS), using the graphite lattice, allowing a more accurate unit cell determination. The images are low-pass filtered. The imaging parameters are indicated in the figure caption: tunneling current (I_{set}), and sample bias (V_{bias}). Distribution of the CW and CCW honeycomb structures (nanowells) on the surface was determined as an average based on at least three different experimental sessions. Each value of surface coverage given in Table 1 and Table S1 was determined by using approximately 10 large scale images (50 × 50 nm²) per session. This method proved satisfactory for confirming the equal probability of the CW and CCW honeycomb structures formed by **DBA-OC10** in achiral solvents. To check the homogeneity of the monolayer structure, several samples were investigated and for each sample several locations on the surface of HOPG were probed.

1. K. Tahara, S. Furukawa, H. Uji-i, T. Uchino, T. Ichikawa, J. Zhang, W. Mamdouh, M. Sonoda, F. C. De Schryver, S. De Feyter, Y. Tobe, *J. Am. Chem. Soc.*, 2006, 128, 51, 16613-16625

2. W.-X. Hong, K.-A. Baker, X. Ma, R. C. Stevens, M. Yeager, Q. Zhang, *Langmuir*, 2010, 26, 8690–8696.

2. Tables

Table S1. Chirality expression for DBA-OC10 in solvent mixtures.

Solvent	Ratio	CCW	CW	Mix	C (mol/l)	# Pores	# Domains	# Images
1-octanol + (*S*)-2-octanol	0/100	**94%**	6%	0%	2.1×10^{-6}	2081	42	32
	50/50	**77%**	23%	1%	2.1×10^{-6}	3413	58	38
	90/10	**56%**	36%	8%	2.1×10^{-6}	2428	98	39
	99/1	**49%**	40%	11%	2.1×10^{-6}	2416	107	38
1-hexanol + (*R*)-2-decanol	0/100	5%	**90%**	5%	2.1×10^{-6}	3169	90	34
	25/75	10%	**86%**	4%	2.1×10^{-6}	3337	103	43
	50/50	6%	**92%**	2%	2.1×10^{-6}	2564	74	38
	75/25	22%	**77%**	2%	2.1×10^{-6}	2678	89	38
	90/10	39%	**58%**	2%	2.1×10^{-6}	2058	106	42
1-decanol + (*S*)-2-hexanol	0/100	**79%**	18%	2%	1.4×10^{-6}	1897	74	31
	25/75	**59%**	36%	5%	2.1×10^{-6}	3656	95	34
	50/50	**51%**	26%	21%	2.1×10^{-6}	3138	182	34
	75/25	26%	35%	39%	2.1×10^{-6}	2829	202	31

3. Conformation of DBAs on surface

DBAs become chiral upon adsorption due to the tilting of the alkoxy chains with respect to the triangular DBA core. As a consequence, the angle between the alkoxy chain and the triangular DBA core (θ) is either larger or smaller than 90° and these conformations are labeled (*R)*-DBA and (*S*)-DBA, respectively.[3] This implies that at the level of a DBA dimer four different arrangements are possible and these lead to four different chiral networks: CCW-(R), CW-(S), CW-(R) and CCW-(S) (as depicted in Fig. S1). Based on experimental data, it seems that the parity (odd or even) of the alkoxy chain determines which chiral network is obtained: odd DBAs exclusively form CCW-(S) and CW-(R), while even DBAs only form CCW-(R) and CW-(S). As a result the monolayers of odd and even DBAs are oriented differently with respect to the layer underneath. The unit cell vectors (red) of **DBA-OCn$_{\mathbf{odd}}$** typically form an angle of ±15° with respect to the normal of graphite (indicated by the orange dashed lines in Fig. S1), while the unit cell vectors of **DBA-OCn$_{\mathbf{even}}$** always form ±5° angles. Due to the tilting, the networks formed by **DBA-OCn$_{\mathbf{odd}}$** and those by **DBA-OCn$_{\mathbf{even}}$** are not mirror image related, but diastereomeric. This intriguing observation can be vital in determining how the chiral solvent transfers its chiral information to the two-dimensional network on the surface.

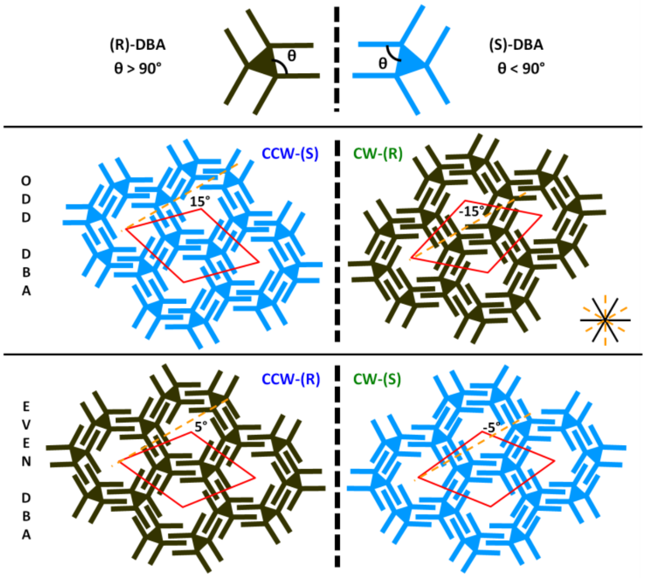


Fig S1. Two prochiral DBAs are formed upon adsorption due to tilting of the alkoxy chains. Depending on whether the angle is θ >90° or θ <90° a (R)-DBA (dark green) or (*S*)-DBA (blue) will be formed, respectively. Combining the molecular chirality with the two possible interdigitation patterns, four different types of dimers and thus also networks can be formed. Unit cells are indicated in red. The normals of graphite are depicted by the dashed orange lines.

[3] E. Ghijsens, O. Ivasenko, K. Tahara, H. Yamaga, S. Itano, T. Balandina, Y. Tobe and S. De Feyter, *ACS Nano*, 2013, 7, 8031.

4. MIX pores

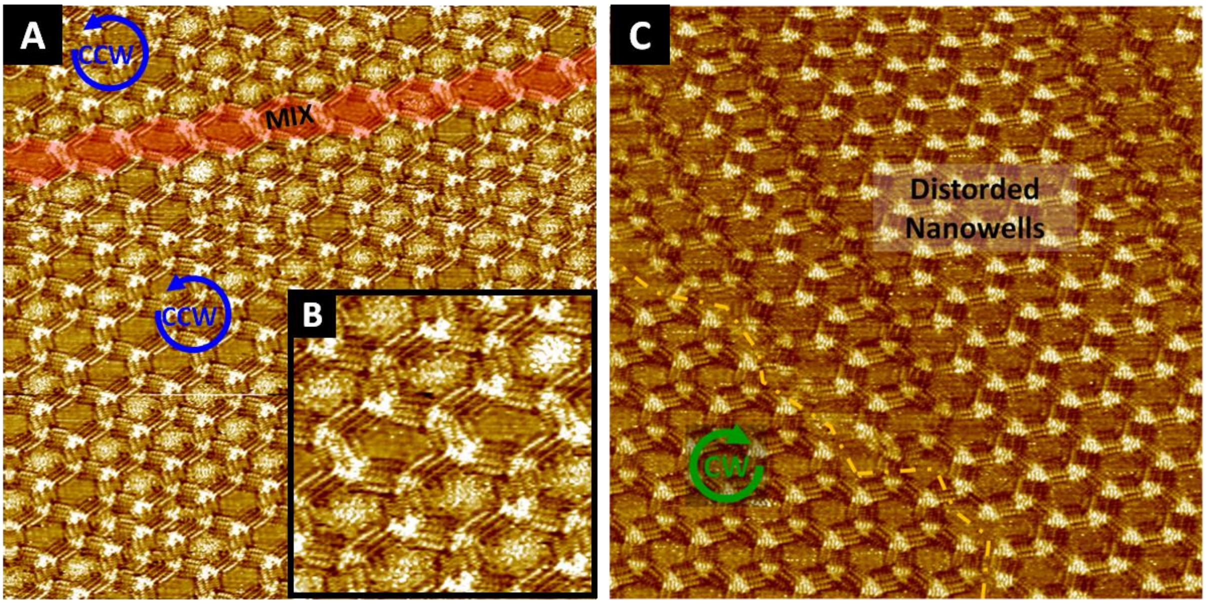


Fig. S2. (A) STM image of **DBA-OC12** at the interface between HOPG and (*S*)-2-octanol. At domain boundaries sometimes lines of MIX nanowells are formed. **(B)** Zoom in of A) **(C)** STM image of **DBA-OC11** showing domains built up from MIX pores.

5. Contamination commercial (*S*)-2-hexanol

If **DBA-OC10** was deposited from unpurified (*S*)-2-hexanol, the surface was frequently covered with unidentifiable compounds and only small patches of DBAs appeared. Analysis of these patches only resulted in a coverage of 58% of induced CCW pores. So clearly, these unidentifiable compounds have a clear impact on the self-assembly behavior. Therefore, we decided to distillate (*S*)-2-hexanol and repeat the experiment, which resulted in the reported value of 79% induced nanowells.

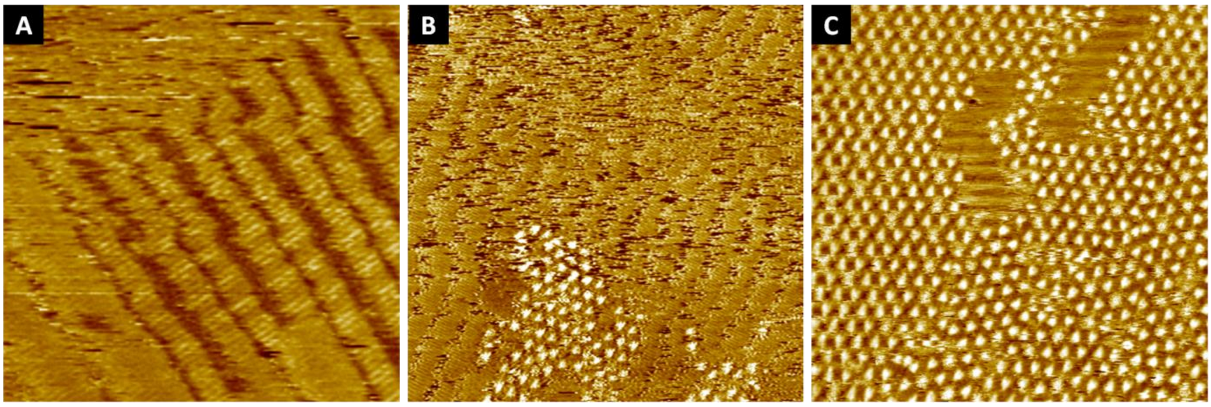
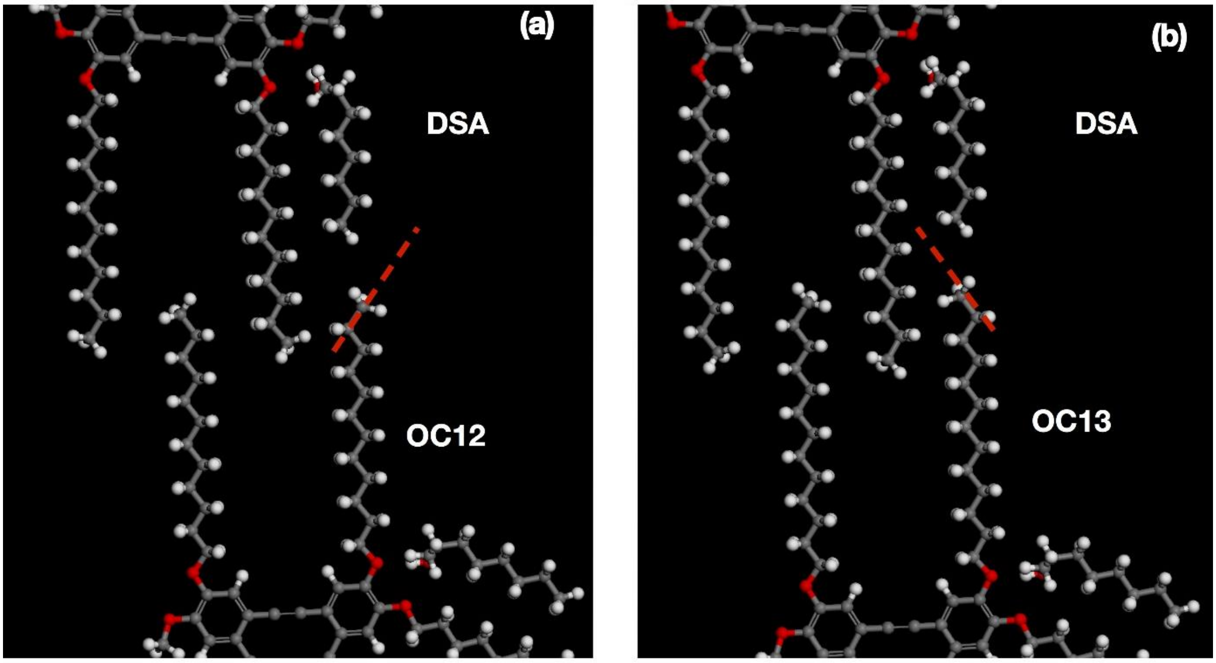


Fig. S3. Alkyl chain containing contamination on the graphite surface after deposition from non-distilled (*S*)-2-hexanol. **(A)** Close up STM images of the contamination. **(B)** The surface is mostly covered with the contamination. Only small DBA domains can be observed. **(C)** STM image of a preheated, concentrated solution revealing larger DBA domains. The contamination is still present.

6. Odd-even effect

We used the computational approach to try to understand why a chiral solvent does not promote a chiral induction in monolayers of DBAs with an odd number of carbon atoms in the alkoxy groups, such as DBA-OC13. OC12 and OC13 groups have opposite orientations of the last bond of the chain. When the number of carbon atoms is even, the last C-C bond of the interdigitating group points towards the center of the DSA site, while for chains with an odd number of carbon atoms, this bond points to the opposite direction, i.e., towards the alkoxy group of the adjacent DBA molecule (fig. S4).



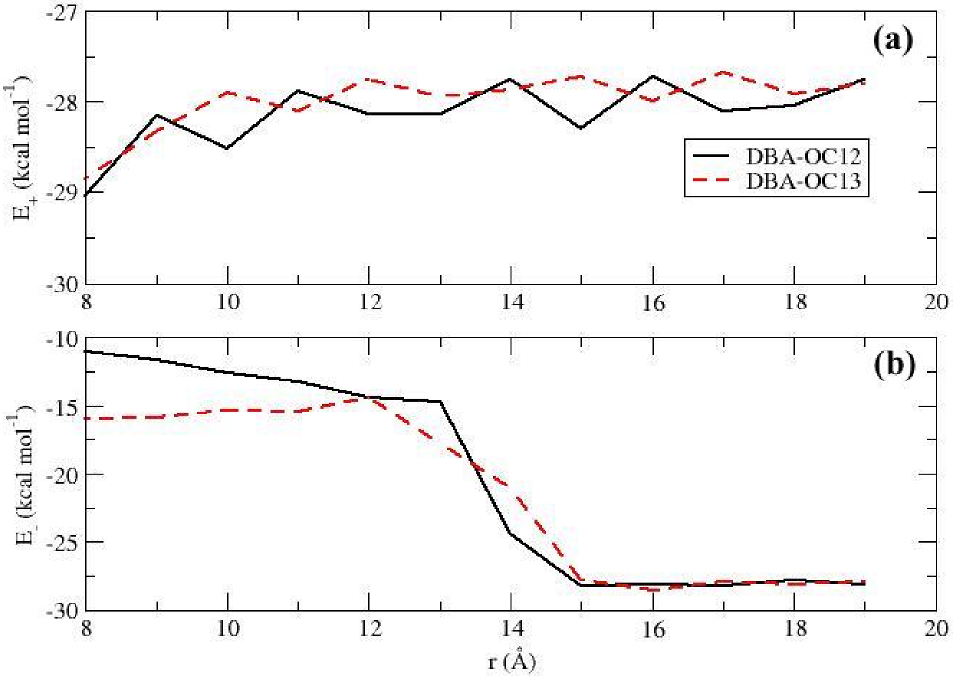


Fig. S4. Top. Orientation of the terminal C-C bond of an even (DBA-OC12) (a) and odd (DBA-OC13) (b) interdigitating alkoxy chain. The dashed line highlights the orientation of the terminal C-C bond. Bottom. Comparison of the interdigitation profiles computed for the favorable (a) and unfavorable (b) interdigitations of DBA-OC12 and DBA-OC13, respectively.

Our hypothesis is that this orientation will make it easier to displace and remove the solvent molecule from the site, hence reducing the energy difference found for DBA-OC13 between favorable and unfavorable interdigitation. To verify this hypothesis, we computed an interdigitation profile for two DBA-OC13 molecules in the presence of a molecule of *(S)*-2-octanol in the DSA site and interacting with IS1. Fig. S4 bottom compares the interdigitation profiles for the + (favorable) and – (unfavorable) interdigitations computed for DBA-OC12 and DBA-OC13, respectively. These interdigitation profiles show that there is no difference for the favorable "+ "interdigitation while for the unfavorable "–" interdigitation for DBA-OC13, from when the solvent molecule starts to hinder the interdigitation (r =15 Å) on, about 5 kcal.mol^{-1} less energy is required with respect to DBA-OC12. Interestingly, after a peak in energy at r = 12 Å, the interdigitation profile of DBA-OC13 shows a plateau with the energy remaining constant, while it always increases in the case of DBA-OC12. Despite the differences in interdigitation profiles, the modeling still predicts chiral induction in case of DBA-OC13.

7. High-density phase

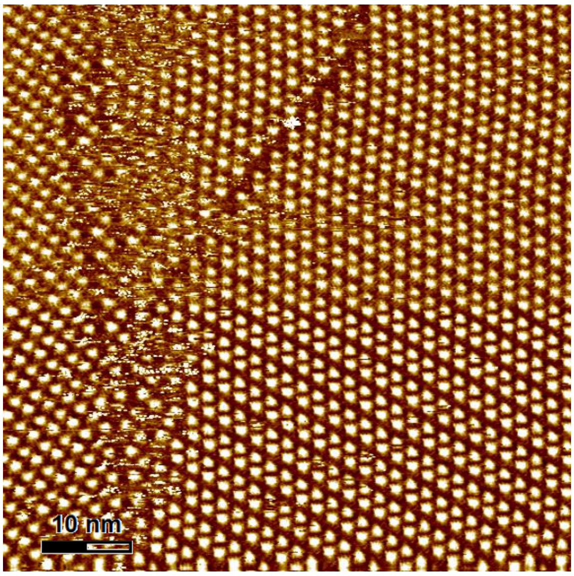


Fig. S5. High-density phase of DBA-OC11 prepared by annealing at the (*S*)-2-octanol / graphite interface.