

Supporting Information

'Sergeants-and-Corporals' principle in chiral induction at an interface

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1. Materials and Methods

All STM experiments were performed at room temperature (20–23°C) using a PicoSPM (Molecular imaging, now Agilent) machine operating in constant-current mode with the tip immersed in the supernatant liquid. STM tips were prepared by mechanical cutting from Pt/Ir wire (80%/20%, diameter 0.2 mm). The porphyrins were synthesized according to the procedure reported in the literature.¹ The solvents 1-heptanol (Fluka 99%), (*S*)-2-octanol (Alfa Aesar 99%) and (*R*)-2-octanol (Alfa Aesar 99%) were used without further purification. Porphyrins were dissolved in these solvents by gentle heating at 60 °C. The concentrations used in each experiment is 0.1mg/1mL. 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). 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 imaging the graphite substrate underneath it under the same experimental conditions, except for lowering the bias. The images were corrected for drift *via* Scanning Probe Image Processor (SPIP) software (Image Metrology ApS), using the recorded graphite images for calibration purposes, 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}).

2. High resolution images of porphyrins 3-4 at the chiral 2-octanol/HOPG interface

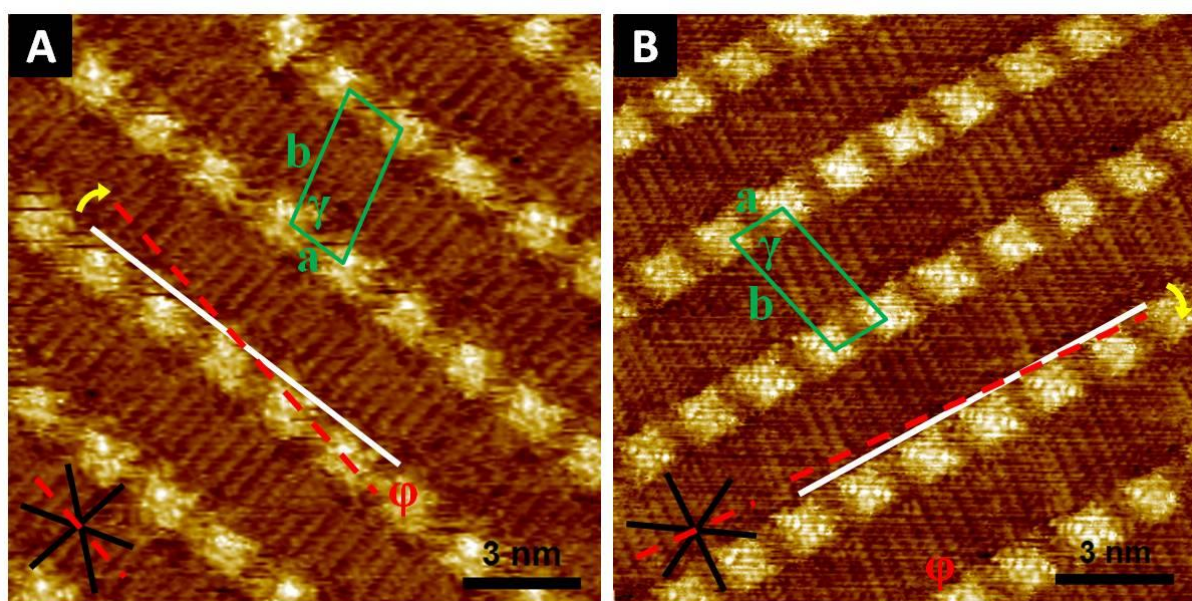


Figure S1. STM images of the chiral porphyrin (*S,S*)-**3** physisorbed at the (A) (*S*)-2-octanol/HOPG interface or (B) (*R*)-2-octanol/HOPG interface. The black solid lines indicate the direction of the main symmetry axes of the underlying graphite. The dashed red lines indicate the reference axis of graphite $\langle -1\ 1\ 0 \rangle$. Unit cells are indicated in green. ϕ is the angle between the reference axis and the unit cell vector *a*. The yellow arrows display the rotation direction. Tunnelling parameters are $I_{\text{set}} = 400$ pA and $V_{\text{bias}} = 210$ mV.

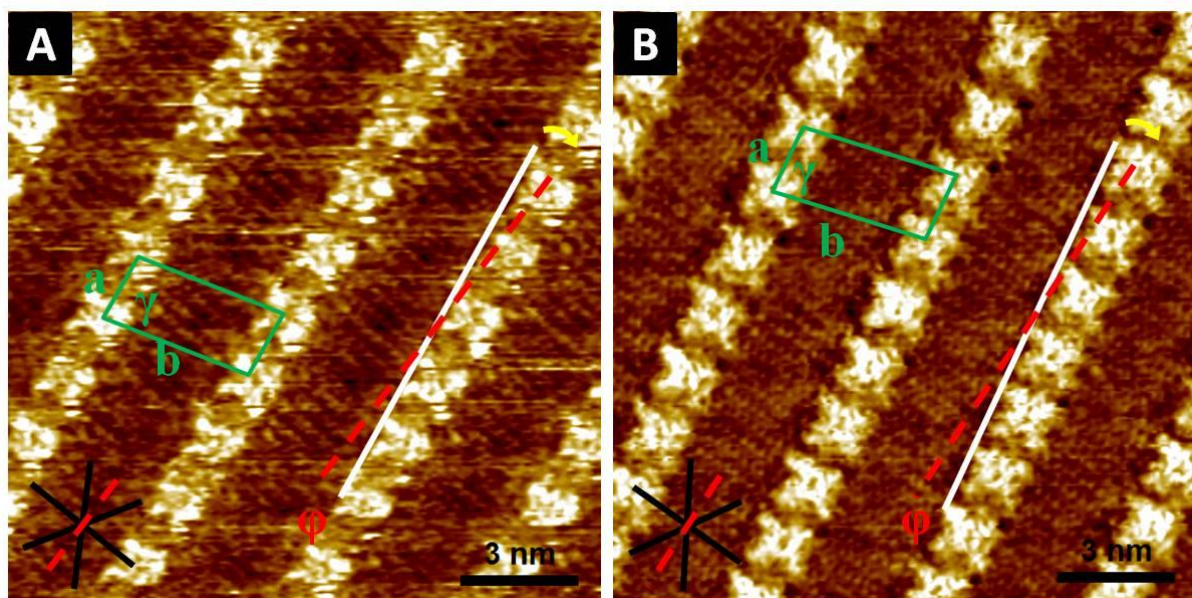


Figure S2. STM images of the chiral porphyrin (*S,S*)-**4** physisorbed at the (A) (*S*)-2-octanol/HOPG interface or (B) (*R*)-2-octanol/HOPG interface. The black solid lines indicate the direction of the main symmetry axes of the underlying graphite. The dashed red lines indicate the reference axis of graphite $\langle -1\ 1\ 0 \rangle$. Unit cells are indicated in green. ϕ is the angle between the reference axis and the unit cell vector *a*. The yellow arrows display the rotation direction. Tunnelling parameters are $I_{\text{set}} = 280$ pA and $V_{\text{bias}} = 230$ mV.