SUPPORTING INFORMATION FOR

Chiral non-periodic surface-confined molecular nanopatterns revealed by scanning tunnelling microscopy

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Contains:

- Full synthetic details
- Description of STM experimental procedures
- Supporting images and analysis
**Experimental Section**

**General Details** The starting materials were purchased commercially and were used without further purification. Thin-layer chromatography (TLC) was performed on aluminium plates coated with Merck Silica gel 60 F254. Developed plates were air-dried and scrutinized under a UV lamp. Silica gel 60 (35-70 mesh, SDS) was used for column chromatography. Melting points were determined by differential scanning calorimetry (DSC) using a Perkin Elmer DSC 7 instrument. $^1$H and $^{13}$C NMR spectra were recorded using the deuterated solvent as lock and tetramethylsilane as internal reference.

**Synthesis**

(R)-Methyl 2-(6-hydroxynaphthalen-2-yloxy)propanoate ((R)-2): 2,6- Dihydroxynaphthalene (3g, 18.73 mmol), (S)-methyl lactate (2.05 mL, 1.2 eq.) and triphenylphospine (3.4g, 1.2 eq.) were dissolved in dry THF (100 mL) and the mixture was cooled in an ice bath to 0ºC under an atmosphere of nitrogen. A solution of diisopropylazodicarboxylate (DIAD, 2.55 mL) in 15 mL of THF was added drop-wise to the stirred solution over 15 minutes and the reaction was stirred overnight at 0ºC. After addition of water (50 mL), the THF was removed in rotary evaporator and the aqueous mixture was extracted twice with dichloromethane. The organic phase was dried over Na$_2$SO$_4$ and purified by column chromatography on silica gel using 10-20 % vol. ethyl acetate in hexane to give 620 mg of product (24% yield). M.F.: C$_{14}$H$_{14}$O$_4$ M.W. 246.26 M.P. 85-87 ºC $[\alpha]^{25}_{546}$ = +10.4 deg.cm$^2$.g$^{-1}$ (C=77 mM CH$_2$Cl$_2$) $^1$H NMR (250 MHz, CDCl$_3$): 7.57-7.48 (m, 2H, ArH), 7.18-7.02 (m, 4H, ArH), 5.48 (br s, 1H, -OH), 4.92 (q, $J=6.8$ Hz, 1H, -OCH$_3$COOCH$_3$), 3.81 (s, 3H, -COOC$_2$H$_5$), 1.70 (d, $J=6.8$ Hz, –OCH$_3$COOMe) ppm. $^{13}$C NMR (62.5 MHz, CDCl$_3$): 173.9, 154.1, 152.9, 130.9, 129.7, 128.9, 128.6, 119.7, 118.8, 110.1, 108.6, 73.2, 53.0, 19.0 ppm. FT-IR (UATR) 3391, 2945, 1726, 1600, 1524, 1470, 1437, 1385, 1327, 1267, 1207, 1179, 1159, 1136, 1114, 1094, 1052, 980, 951, 850, 802, 748, 692 cm$^{-1}$.
(S)-Methyl 2-(6-hydroxynaphthalen-2-yl oxy)propanoate ((S)-2). The preparation was carried out in same way as for the enantiomer. [α]^{25}\_\text{546} = -11.3 \text{deg.cm}^2\text{.g}^{-1} (C=47 \text{mM CH}_2\text{Cl}_2) The rest of the analytical data was identical to that of the (R) enantiomer.

(R)-Methyl 2-(6-(octadecyloxy)naphthalen-2-yloxy)propanoate ((R)-3). Pre-dried and ground K$_2$CO$_3$ (1.1 g, 4 eq.) was suspended in acetonitrile (30 mL) in a 3 neck round bottom flask and the mixture was degassed with a flow of nitrogen for 30 minutes. Then (R)-methyl 2-(6-hydroxynaphthalen-2-yloxy)propanoate ((R)-2) (480 mg, 2.01 mmol) was added as a solid, and the resulting solution was heated to reflux under nitrogen. After 30 minutes, the reaction was cooled, and 1-bromooctadecane (0.71 mL, 1.05 eq) was introduced as a liquid. The temperature of the mixture was then raised to gentle reflux, and these conditions were maintained for 48 hours. The reaction mixture was filtered at the pump while it was still warm, and the residual solid was washed with warm acetonitrile. Immediately crystals had started to form in the liquid, and after 30 minutes they were collected by next filtration. After evaporating some of acetonitrile with a rotary evaporator from filtrate, a further crop of crystals was obtained. Reaction gave 720 mg of white solid (yield 74%). M.F.: C$_{37}$H$_{50}$O$_4$ M.W. 498.74 M.P. 78-79 ºC [α]^{25}\_\text{546} = +4.12 \text{degcm}^2\text{.g}^{-1} (C=15 \text{mM CH}_2\text{Cl}_2)

$^1$H NMR (360 MHz, CDCl$_3$): 7.64-7.59 (m, 2H, ArH), 7.20-7.02 (m, 4H, ArH), 4.90 (q, $J = 6.8$ Hz, 1H, -OCH$_2$CH$_3$COOMe), 4.06 (t, $J = 6.6$ Hz, 2H -OCH$_2$(CH$_2$)$_{16}$CH$_3$), 3.78 (s, 3H, -COOC$_3$H$_3$), 1.90-1.80 (m, 2H, -OCH$_2$CH$_2$(CH$_2$)$_{15}$CH$_3$), 1.69 (d, $J=6.8$ Hz, -OCH$_2$CH$_2$COOMe), 1.50-1.40 (m, 2H, -OCH$_2$CH$_2$CH$_2$(CH$_2$)$_{14}$CH$_3$), 1.40-1.20 (m, 28H, -O CH$_2$CH$_2$CH$_2$(CH$_2$)$_{14}$CH$_3$), 0.90 (t, $J=6.8$ Hz, 3H, -O(CH$_2$)$_{17}$CH$_3$) ppm. $^{13}$C NMR (90 MHz, CDCl$_3$): 172.8, 155.9, 153.8, 130.2, 129.3, 128.3, 128.1, 119.4, 119.0, 108.1, 106.7, 72.7, 68.0, 52.3, 31.9, 29.7, 29.3 26.0, 22.6, 18.6, 14.1 ppm. FT- IR
(S)-Methyl 2-((6-(octadecyloxy)naphthalen-2-yloxy)propanoate ((S)-3). The preparation was carried out in same way as for the enantiomer. $[\alpha]^{25}_{546} = -4.44 \text{ deg cm}^2\text{g}^{-1}$ (C=21 mM CH$_2$Cl$_2$)

The rest of the analytical data was identical to that of the (R) enantiomer.

(R) 2-((6-(Octadecyloxy)naphthalen-2-yloxy)propanoic acid ((R)-1). To a solution of an ester (680 mg) in Methanol (50 mL) was added 2N water solution of sodium hydroxide (4eq. ~2mL) and the mixture was stirred overnight at room temperature. The reaction mixture was concentrated, diluted with water and acidified to pH=2 with 2N hydrochloric acid. The acid compound was extracted with DCM two times and crystallized from acetonitrile to give 455 mg of the desired product. (Yield 69%) M.F.: C$_{36}$H$_{48}$O$_4$ MALDI-TOF MS m/z: calc. 484.36 found 484.30 P. 104-105°C. $[\alpha]^{25}_{546} = -4.82 \text{ deg cm}^2\text{g}^{-1}$ (C=12 mM CH$_2$Cl$_2$) $^1$H NMR (360 MHz, CDCl$_3$): 7.66-7.60 (m, 2H, ArH), 7.20-7.08 (m, 4H, ArH), 4.93 (q, $J$=6.8 Hz, 1H, -OCH$_{2}$COOH), 4.06 (t, $J$=6.5 Hz, 2H -OC$_2$H$_7$(CH$_2$)$_{16}$CH$_3$), 1.90-1.80 (m, 2H, -OCH$_2$CH$_2$(CH$_2$)$_{15}$CH$_3$), 1.72 (d, $J$=6.8 Hz. –OCH$_3$COOMe), 1.50-1.40 (m, 2H, -OCH$_2$CH$_2$CH$_2$(CH$_2$)$_{14}$CH$_3$), 1.40-1.20 (m, 28H, -OCH$_2$CH$_2$CH$_2$(CH$_2$)$_{14}$CH$_3$), 0.90 (t, $J$=6.8 Hz, 3H, -O(CH$_2$)$_{17}$CH$_3$) ppm. $^{13}$C NMR (90 MHz, CDCl$_3$): 176.1, 156.1, 153.4, 130.5, 129.3, 128.5, 128.2, 119.6, 118.9, 108.8, 106.9, 72.5, 68.1, 31.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 22.7, 18.4, 14.1 ppm. FT-IR (UATR) 3576, 2917, 2850, 1724, 1604, 1509, 1463, 1395, 1309, 1232, 1167, 1120, 1137, 1120, 1035, 972, 953, 848, 809, 792, 753, 718, 661 cm$^{-1}$. 


Electronic Supplementary Material (ESI) for CrystEngComm
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(R) 2-(6-(Octadecyloxy)naphthalen-2-yloxy)propanoic acid ((S)-1). The preparation was carried out in same way as for the enantiomer. \( [\alpha]^{25}_{546} = -5.3 \, \text{deg cm}^2 \text{g}^{-1} \) (\( C=6.9 \, \text{mM CH}_2\text{Cl}_2 \)). The rest of the analytical data was identical to that of the (R) enantiomer.

**Scanning Tunnelling Microscopy.** STM images presented here were obtained at the liquid-solid interface using a PicoSPM (Agilent). STM tips were mechanically cut from Pt/Ir wire (80%/20%, diameter 0.2 mm). Highly oriented pyrolytic graphite (HOPG, grade ZYB, Advanced Ceramics Inc., Cleveland, OH) was used as a substrate. An almost saturated solution of the compound in 1-phenyloctane (Aldrich, 99%) was prepared and heated for about 10 minutes at 70 °C prior to applying a drop of this solution to the basal plane of freshly cleaved HOPG. After about half an hour, the STM tip was immersed into the solution and scanned in the variable height mode. The setpoint current \( (I_{\text{set}}) \) is typically smaller than 0.5 nA. The bias voltage was \( (V_{\text{bias}}) \) applied to the sample in such a way that at negative bias voltage electrons tunnel from the sample to the tip. For analysis purposes, the imaging of a molecular layer was immediately followed by recording at a lower bias voltage the graphite lattice, under otherwise identical experimental conditions. Drift effects were corrected for using Scanning Probe Image Processor (SPIP) software (Image Metrology ApS). Note that only images containing a small drift were used for analysis.
Cumulative 'up'-'down' sequence.

Figure of cumulative sequence of 'up'-'down' trend for (S)-1, for all domains analyzed (more than 1500 up-down events), showing that the effects seen for one domain (Figure 3) are repeated over large domains and all areas of the monolayer.