Macroscopic, Hierarchical Surface Patterning of Porphyrin Trimers via Self-Assembly and Dewetting

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One sentence summary: By means of spontaneous self-assembly and evaporation phenomena, macroscopic linear patterns of dye molecules on mica and glass surfaces can be obtained that are capable of aligning liquid crystal molecules.

Abstract: The use of bottom-up approaches to construct patterned surfaces for technological applications is appealing, but to date applicable to only relatively small areas (~10 µm²). We constructed highly periodic patterns at macroscopic length scales, in the range of square millimeters, by combining self-assembly of disk-like porphyrin dyes with physical dewetting phenomena. The patterns consist of equidistant 5 nanometer wide lines spaced 0.5 to 1 micrometers apart, comprising single porphyrin stacks containing millions of molecules, and are formed spontaneously upon drop-casting a solution of the molecules onto a mica surface. On glass, thicker lines are formed which can be used to align liquid crystals in large domains of square millimeters.

The formation of complex submicrometer patterns on surfaces that extend over macroscopic distances underlies the fabrication of integrated circuits and microelectromechanical devices (1-3). However, for many applications, such as detection arrays and optical elements, well-defined symmetrical patterns can be exploited, especially if the methods decrease the number of processing steps needed or avoid surface invasive steps that scratch, rub, or etch the surface. Examples of complex pattern formation by non-invasive techniques are still few, usually require large polymeric molecules, and are often of small spatial extent (4-12). Self-assembly of molecules on a surface can be a simple, versatile and less time consuming approach and may lead to defect free structures (1), especially if combined with physical processes such as dewetting and contact line pinning. Here we report the spontaneous formation of periodic patterns of exceptionally long (up to 1 mm) columnar stacks of porphyrin dye molecules at a solid-liquid interface, with a highly
defined spatial and parallel ordering. These self-assembled patterns were then used to align liquid crystals (LCs) in domains of several square millimeters.

Porphyrin dye molecules can self-organize on a surface into small columnar stacks of submicrometer length (13, 14). These architectures are generated as a result of combined self-assembly and dewetting, which take place simultaneously when a dropcasted solution of the porphyrin molecules is evaporated on the surface. In order to enhance the columnar stacking and hence the length of the assemblies, we have synthesized compound 1 (Fig. 1) (15), which consists of three porphyrin moieties, that are linked via amide bonds to a central benzene core, a motif which is known to form extended hydrogen bonded networks (16-19). Each porphyrin is equipped with three aliphatic hydrocarbon chains to increase the solubility of the stack in organic solvents.

The high tendency of 1 to form aggregates can be directly observed in that at a concentration of 8 mg/ml, the chloroform solution formed a gel. This strong aggregation is highly dependent on the presence of the alkyl chains, since porphyrin trimers without these chains appeared not to gelate the solvent. In the proton nuclear magnetic resonance (NMR) spectrum of 1 in CDCl₃ ([I] = 10^⁻⁴ M), very broad peaks were observed, suggesting large aggregate formation. The addition of d⁶-DMSO to this solution caused a sharpening of the NMR signals, which is the result of the solvent breaking up the hydrogen-bonding network (Fig. 1D) and dissolving the aggregates present in chloroform.

At the solid-liquid interface, the expected columnar stacking of 1 was confirmed by means of scanning tunneling microscopy (STM) (Fig. S1). The aggregation behavior at a surface was further studied with atomic force microscopy (AFM). We drop-casted a diluted solution of 1 in chloroform ([I] = 4.8 × 10⁻⁶ M, 3 µl droplets) on mica. After evaporation, very large domains (up to ~ 3 mm²) containing a highly ordered pattern of equidistant nearly parallel wire-like architectures were observed (Fig. 2, A and B). The height of the lines was 4.5 ± 0.4 nm (Fig. 2C), which corresponds remarkably well to the calculated diameter of 1, indicating a pronounced shape persistence of the molecule. These observations indicate that the lines consist of a columnar stack one molecule thick, and each of the lines containing millions of molecules. We will argue below that this self-organization of molecules on a macroscopic scale results from a hierarchical dewetting process.

Analysis of several samples revealed a narrow spatial distribution of the periodicity within one single domain (e.g. 650 ± 40 nm in a domain with a size of 3 mm², Fig. 2D), but between several domains the value of the periodicity varied from 0.5 to 1 µm. The lines were oriented parallel with respect to the local solvent front, which can be deduced from the broader contact pinning lines on the sample (see below, Fig. 2E). In addition, at the boundaries of these ordered domains, patterns more reminiscent of normal spinodal dewetting were observed (Fig. 2F). A clear correlation is seen between these two regions,
because most columns in the periodic domain appear to grow out from the spinodal dewetting domain.

When larger droplets ([I] = 4.8 × 10^{-6} M, 10 µl) were deposited under similar conditions, the longer evaporation time formed porphyrin lines with different dimensions and orientations from those described above (Fig. 3A). Now, a periodicity of 13.4 ± 0.7 µm and a line height of 55.4 ± 0.6 nm were observed. The latter value indicates that each line in this pattern consist of a bundle of columnar stacks of I. Because of the larger dimensions, this pattern could be visualized via optical microscopy (Fig. 3B), which clearly demonstrated that the orientation of the lines, which are up to 0.8 mm long (Fig. S3), is now orthogonal with respect to the solvent front (see below). Scanning confocal fluorescence microscopy studies (Fig. 3C, excitation λ = 411 nm) confirmed that the lines consist of molecules of I and an emission spectrum characteristic of a porphyrin aggregate (I3) was obtained (inset Fig. 3C).

Because mica is birefringent, we could not study the assembly processes optically in real time. We could, however, visualize the line-formation process in real time on a glass surface ([I] = 4.8 × 10^{-5} M, 10 µl), using an optical polarization microscope equipped with a CCD camera (Movie S1). During the evaporation process, the front of the droplet was pinned several times, and upon its withdrawal, deposited material was observed (Fig. 3D). Simultaneously with the pinning, the formation of linear aggregates as a result of the self-assembly processes was already visible within the droplet, perpendicular to the front, before its withdrawal (Fig. S2 and Movie S1). However, the greater roughness of the glass substrate compared to mica caused the pattern to be less well-defined.

The formation of the highly ordered line patterns is governed by a combination of molecular self-assembly and other physical processes (I3). The strong self-assembly of I, which is governed by a balanced combination of hydrogen bonding and π-π stacking interactions, is essential for the growth of columnar stacks of almost millimeter length. None of a wide family of porphyrin macrocycles (hexamers, dodecamers and porphyrin trimers with ester instead of amide linkers) were able to form similar periodic patterns (I3).

The two primary physical processes that play a major role in pattern formation are contact line pinning between the edge of a droplet and the surface – the so-called “coffee-stain mechanism” – and spinodal dewetting (9, 20-24). The latter effect is observed when the surface of a thin film on a flat substrate (viz. mica) is unstable and deforms spontaneously. Surfaces subject to such kind of dewetting are known to dewet via the formation of an undulating bicontinuous pattern (24). We postulate that this undulating pattern governs the spatial distribution of the linear aggregates (Fig. 3E). The small defects observed in Fig 2A support this postulation, because their presence does not interrupt the periodicity of the patterns.

The initial physical phenomenon, contact line pinning and solvent evaporation, causes a flow of the molecules dissolved in the droplet toward the contact line (9). In the case of the
small droplets (3 µL), the contact line is pinned several times, leaving behind thin layers of deposited molecules of 1 at these positions (Fig. 2, E and G) (9). After repeated retractions of the solvent front, thin films remain between the pinned contact lines, which are then subject to spinodal dewetting. Combined with the propensity of 1 to form 1D aggregates, this dewetting gives rise to the formation of the highly defined periodic patterns, with the contact pinning lines directing their orientation (Fig. 2G). Within each domain, the local spinodal dewetting determines the periodicity, which is in all cases between 500 nm and 1 µm.

In the case of the larger droplets (10 µL), the evaporation of the solvent takes longer and allows the formation of larger aggregates already in solution, which are subsequently deposited (Fig. 3, A and B). Apparently, there is not enough material present at the contact line to completely pin it (9). The resulting partial pinning of the solvent front hinders the retraction of the contact line, and in contrast to the experiments with the smaller droplets, contact pinning lines are now not formed (Fig. 3F) (9). The partial pinning causes a flow of molecules toward and orthogonal to the contact line. The concomitant local increase in concentration of molecules of 1 leads to growth of the lines from a direction opposite to the molecular flow, resulting in an orthogonal orientation with respect to the solvent front. The combination of (i) the tendency of the molecules to form 1D aggregates, (ii) the occurrence or not occurrence of contact line pinning, and (iii) spinodal dewetting effects results in the observed surface patterning in the two cases.

Previous reports have described organized assemblies of polymers (24), dendrimers (3, 26-27) and block copolymers (28), leading to crystal-like domains on surfaces. In none of these cases, however, 1D single molecular stacks spontaneously organized into periodic dissipative patterns have been observed. Unlike in our case, constructing such patterns requires invasive techniques such as lithography or sliding glass plates (29, 30).

The line patterns obtained with the large droplets were investigated as possible LC alignment layers. Liquid crystal cells, consisting of one glass plate covered with the aggregates and a non-rubbed counter plate spin-coated with a commercially available polyimide, were prepared and filled with 4-cyano-4’-pentyl biphenyl (5CB) molecules in the isotropic phase to avoid flow alignment. Polarizing microscopy showed that the cells contained aligned LC domains of several square millimeters (Fig. 4) in the regions of the linear aggregates and no alignment in other areas. Closer inspection showed that the alignment was interrupted by concentric circles, which are the contact pinning lines (Fig. 3D).

Interestingly, the contact pinning lines themselves do not align the LC molecules, but remain visible, which indicates that the formed aggregates are the ones that act as a command layer. Second harmonic generation (SHG) measurements confirmed that the mesogenic molecules were uniformly aligned parallel to the radially oriented stacks of 1, i.e. perpendicular to the contact lines, in exceptionally large domains (1 cm², Fig. 4). As for
most anisotropic surfaces that show LC alignment (31), the alignment is probably due to (i) a minimization of elastic energy and (ii) the presence of molecular interactions between the LC molecules and the oriented columnar stacks (32). In the case of the ordered porphyrin patterns, however, especially dipole-dipole interactions are expected to have a large effect, since the head-to-tail orientation of the amide functions within the linear aggregates, as shown in Fig. 1D, creates a macroscopic dipole moment parallel to the stacking axis (17). The use of periodic patterns created by controlled self-organization may lead to a viable and cheap alternative to current methods of forming alignment layers.

The remaining challenge in exploiting this phenomenon will now be to further control the self-assembly in such a way that surface patterns can be oriented at will. Control over the periodic arrays might be accomplished by patterned heating of the surface using laser gratings or by applying an electric field to align the high intrinsic dipole moments of the stacks. Extra stabilization of the patterns can be achieved by introducing cross-linkable groups (e.g. cinnamate, thiophene, or methacrylate units) in the alkyl chains, which would allow post-modification of the patterns after their deposition on the surface. The self-assembly/dewetting technique could also be applied in conjunction with conventional (photo-)lithographic or stamping methods.

References:
15. Materials and methods are available as supporting material on Science Online.
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Fig. 1. Porphyrin trimer 1. (A) Chemical structure of 1. (B) Schematic representation of 1. (C) Schematic representation of a columnar stack of 1. (D) Computer generated model of the hydrogen bonding network in a columnar stack of 1 (two of the three porphyrins of each molecule of 1 are omitted for clarity).
Fig. 2. Patterns formed on mica after evaporation of 3 µL droplets of compound 1 in chloroform. (A) AFM image (scan size = 25 x 25 µm²) of a pattern of highly ordered equidistant parallel lines. (B) AFM image (scan size = 10 x 10 µm²) with the inset showing the cross-section indicated in the AFM image. (C) Bar diagram showing the height distribution of the line pattern within a single domain, with the Gaussian fit demonstrating a line height of 4.5 nm, with σ = 0.4 nm. (D) Bar diagram showing the spatial distribution of lines in a single domain (size = 3 mm²). Each color represents a different position in a single domain. The Gaussian fit demonstrates that within this complete domain the lines are 650 nm apart and σ = 40 nm. (E) AFM image (scan size = 14 x 14 µm²) showing that the periodic pattern is parallel to the (bold) contact pinning line. (F) AFM image (scan size = 40 x 40 µm²) of a domain-transition between a highly ordered and a less ordered domain. (G) Mechanism of the formation of the patterned lines. During the evaporation of the droplet (A→B), the contact line is pinned several times, resulting in the formation of contact pinning lines (designated with 1, 2 and 3). After retraction of the solvent front, a thin film remains in which a pattern of thin lines is formed as a result of self-assembly and dewetting.
Fig. 3. Patterns formed after evaporation of 10 µl droplets of compound 1 in chloroform. (A) AFM image (scan size = 95 x 95 µm²) of a line pattern on mica. (B) Optical micrograph of the pattern formed on mica (scale bar = 100 µm). (C) Scanning confocal fluorescence microscopy image of the lines; the inset shows the characteristic fluorescence spectrum of a porphyrin aggregate, $\lambda_{\text{max} 1} = 665$, nm $\lambda_{\text{max} 2} = 726$ nm. (D) Optical micrograph of the ‘coffee-stain-like’ pattern formed during the evaporation of a solution of 1 in chloroform on glass ([1] = 4.8 x 10⁻⁵ M); the bottom part is still covered with solution (dark blue). The whitish stripes are the aggregates which remain after retraction of the droplet. (E) Proposed formation of periodic patterns on flat mica; spinodal dewetting causes an undulating pattern in the solvent, which governs the positioning of the aggregates and thus the spatial distribution of the lines. (F) Mechanism of the formation of the patterned lines. The presence of aggregates preformed in solution hinders the retraction of the solvent front from 1 to 2, causing partial pinning of the contact line. In combination with the molecular self-assembly, this partial pinning results in an orientation and growth of linear aggregates orthogonal to the local solvent front; contact pinning lines are not observed.
Fig. 4. Application of the patterns formed by 1 on a glass substrate as alignment layers for 5CB; polarizing microscopy images of a liquid crystal cell between crossed polarizers (denoted by P and A). (A) LC ordering parallel to the analyzer. (B) Texture after rotation of the sample over 45°. The local orientation of the 5CB molecules, deduced from the SHG rotational anisotropy patterns (insets), is depicted schematically in both images.
Supporting Online Material

Supplementary Methods

General.
Dichloromethane and chloroform were distilled from CaH₂ prior to use. All commercial chemicals were used as received. Acros silica gel 60 (size 0.035 – 0.070 mm, pore size 6 nm) was used for column chromatography, BioRad BioBeads SX-1 were used for size-exclusion chromatography.

Instrumental.
NMR-spectra were recorded on Bruker DPX200, Bruker AC300 or Varian Inova400 instruments. Chemical shifts are reported in ppm downfield with respect to the internal standard TMS. Maldi-TOF spectra were measured on a Bruker Biflex III spectrometer in reflection mode. The samples were prepared by mixing 10 μl of dilute solutions of the porphyrin molecules in chloroform with equal amount of matrix solution (dithranol; 20 mg/ml in chloroform) and a droplet of this mixture was put on a sample plate. Elemental analyses were determined with a Carlo Erba Ea 1108 instrument.

Synthesis of compound 1.
Compound 1 was synthesized as shown in scheme 1

Scheme 1. Porphyrin 1 was synthesized in 3 steps. First, 5-p-nitro-10,15,20-tri-p-dodecoxyporphyrin 2 was synthesized, of which the nitro-group was reduced to give an amine 3. Finally, the 3 porphyrins were coupled to the trimesoylchloride to yield 1.
**p-Dodecoxybenzaldehyde**

*p*-Dodecoxybenzaldehyde was synthesized according to a literature procedure (ref 11).

**21H,23H-5-*p*-Nitrophenyl-10,15,20-tri-*p*-dodecoxyphenylporphyrin (2)**

*p*-Dodecoxybenzaldehyde (8.0 gr, 27.5 mmol), *p*-nitrobenzaldehyde (2.0 gr 13.77 mmol) and pyrrole (2.4 gr, 41.3 mmol) were dissolved in propionic acid (250 ml) and refluxed for 2h. The solvent was removed under vacuum and the product purified using column chromatography (eluent dichloromethane), yielding a purple solid. Yield: 4%.

$^1$H-NMR (CDCl$_3$, 300 MHz): $\delta = 8.92$ (d, 2H, $\beta$-pyrrole $J = 4.7$ Hz), 8.89 (s, 4H, $\beta$-pyrrole), 8.72 (d, 2H, $\beta$-pyrrole $J = 4.9$ Hz), 8.63 (d, 2H, CH ortho-Ph-NO$_2$, $J = 8.8$ Hz), 8.40 (d, 2H, CH meta-Ph-NO$_2$, $J = 8.8$ Hz), 8.11, 8.10 (dd, 6H, CH ortho-Ph-OC$_{12}$H$_{25}$, $J = 8.6$ Hz), 7.28 (d, 6H, CH meta-Ph-OC$_{12}$H$_{25}$, $J = 8.6$ Hz). 4.26 (t, 6H, OCH$_2$CH$_2$C$_{10}$H$_{21}$), 1.99 (m, 6H, OCH$_2$CH$_2$C$_{10}$H$_{21}$), 1.63 (m, 6H, OC$_2$H$_4$CH$_2$C$_9$H$_{19}$), 1.36 (broad, 48H, OC$_3$H$_6$C$_8$H$_{16}$CH$_3$), 0.90 (broad, 9H, O-C$_{11}$H$_{22}$CH$_3$), -2.65 (s, broad, 2H, NH-porphyrin).

**21H,23H-5-*p*-Aminophenyl-10,15,20-tri-*p*-dodecoxyphenylporphyrin (3)**

SnCl$_2$.H$_2$O (0.5 gr, 2.0 mmol) and 2 (300 mg, 0.25 mmol) were dissolved in 200 ml of HCl-saturated diethyl ether. The mixture was stirred for 48 h. in the dark at room temperature, and afterwards, 200 ml of 3M aqueous NaOH was added. The organic layer was separated and washed with successively an aqueous sat. NaHCO$_3$ solution, with brine (3x), and dried over MgSO$_4$. After removal of the solvent a purple solid was obtained, which was purified by column chromatography (eluent toluene). Yield: 95%.

$^1$H-NMR (CDCl$_3$, 200 MHz): $\delta = 8.95$ (m, broad, 8H, $\beta$-pyrrole), 8.13 (d, 6H, CH ortho-Ph-OC$_{12}$H$_{25}$, $J = 8.4$ Hz), 8.00 (d, 2H, CH meta-Ph-NH$_2$, $J = 8.2$ Hz), 7.25 (d, 6H, CH meta-Ph-OC$_{12}$H$_{25}$, $J = 8.3$ Hz), 6.99 (d, 2H, CH ortho-Ph-NH$_2$, $J = 8.3$ Hz), 4.20 (t, 6H, OCH$_2$C$_{11}$H$_{23}$), 3.90 (s, broad, 2H, NH$_2$), 1.97 (m, 6H, OCH$_2$CH$_2$C$_{10}$H$_{21}$), 1.63 (m, 6H, OC$_2$H$_4$CH$_2$C$_9$H$_{19}$), 1.36 (m, 48H, OC$_3$H$_6$C$_8$H$_{16}$CH$_3$), 0.96 (m, 9H, O-C$_{11}$H$_{22}$CH$_3$), -2.65 (s, broad, 2H, NH-porphyrin).

$^{13}$C-NMR (CDCl$_3$, 50MHz): $\delta = 158.86$ (C-OC$_{12}$H$_{25}$), 145.88 (C-NH$_2$), 135.55 (meta-Ph-OC$_{12}$H$_{25}$), 134.43 (meta-Ph-NH$_2$), 130.88 (broad, CH $\beta$-pyrrole), 113.35 (ortho-Ph-NH$_2$), 112.61 (ortho-Ph-OC$_{12}$H$_{25}$), 68.22 (O-CH$_2$C$_{11}$H$_{23}$), 31.96, 29.69, 29.54, 29.48, 29.41, 26.23, 22.73 (all, -CH$_2$), 14,17 (CH$_3$).

**Porphyrin trimer (1)**

Compound 3 (285 mg 0.24 mmol) and a drop of distilled pyridine were dissolved in dichloromethane under nitrogen atmosphere. At 0°C, trimesoylchloride (17.8 mg, 0.07 mmol) was added and the mixture stirred for 2 hrs, while the solution was allowed to warm to room temperature. The solvent was removed under vacuum and the product was purified by column chromatography (eluent: 1% methanol in chloroform) followed by a size-exclusion chromatography (eluent: toluene). Yield: 90 %.

$^1$H-NMR (toluene-d7 with a droplet of DMSO-d6, 400 MHz): $\delta = 9.59$ (s, broad, 3H central benzene), 9.09 (d, broad, 6H, $\beta$-pyrrole {3 and 7 position of the porphyrin}, $J = 5.1$ Hz),
9.01 (d, 6H, broad, β-pyrrole {2 and 8 position of the porphyrin}, J = 5.2 Hz), 8.99 (s, broad, 12H, β-pyrrole {12, 13 and 18 position of the porphyrin}), 8.84 (d, 6H, CH meta-Ph-NH, J = 8.4 Hz), 8.32 (d, 6H, CH ortho-Ph-NH, J = 8.5 Hz), 8.19 (d, 18H, CH ortho-Ph-OC_12H_25, J = 8.4 Hz), 7.22 (d, 18H, CH meta-Ph-OC_12H_25, J = 8.5 Hz), 3.99 (t, 18H, OC_2H_2C_11H_23, J = 5.9 Hz), 1.84 (m, 18H, CH meta-Ph-OC_12H_25), 1.28 (m, 144H, OC_3H_6C_8H_16CH_3), 0.88 (broad, 27H, O-C_11H_22CH_3), -2.26 (s, broad, 6H, NH-porphyrin).

^13^C-NMR (CDCl_3 with a droplet of DMSO-d6, 50MHz): δ = 164.24 (3C, C=O), 161.64 (C-C =O central benzene ), 137.83, 136.36, 134.77 (all, CH central benzene), 134.79 134.77, 134.41, 134.06 (all, broad, CH ortho-Ph-NH), 132.58, 132.37 (both CH meta-Ph-OC_12H_25), 129.83 (broad, CH β-pyrrole), 118.71, 188.56, 118.26, 117.85 (all, CH meta-Ph-NH), 111.61, 111.35 (both broad, CH ortho-Ph-OC_12H_25), 66.90, 66.72 (both, OCH_2C_11H_23), 30.53 28.27 28.05 27.98 24.83 21.31 (all -CH_2-),12.92 (CH_3).

MALDI-TOF: M^+ = 3702.9. Elemental analysis: Calculated for C_{249}H_{306}N_{15}O_{12}.H_2O: C (80.35), H (8.42), N (5.64). Found: C(80.09), H(8.33), N(5.59).

Atomic Force Microscopy.
For AFM measurements Nanoscope IV and Nanoscope III multimode instruments (Veeco / digital instruments, Santa Barbara, California) equipped with a 12 μm (E scanner) and a 125 μm scanner (J scanner) were used.
Tapping in air was performed with 100 μm long standard silicon tips (NSG 10, ND-MDT, Moscow, Zelenograd, Russia) with average nominal resonant frequencies of 255 kHz and average nominal force constants of 11.5 N/m. Scanning was performed at a speed of 1-2 lines/s with amplitude setpoints of 1.5 – 2 V. Standard software (Nanoscope, version 5.12r5) was used for image processing (1st and 2nd order flattening) and analysis. A droplet (3 or 10 μl) of a solution of 1 in chloroform was placed onto freshly cleaved mica. After evaporation of the solvent the sample was measured by tapping mode AFM.

Statistics.
The spatial distribution within a single domain was determined by performing AFM measurements in 3 areas “far” apart (distance = 0.5 mm). All these measurements were combined and analysed with help of a Gaussian fit (Origin 6.1), which yielded a Gaussian distribution with: R^2= 0.9965, x_0 (centre of the peak) = 652.0 ± 1.0 nm and w (w/2 = σ) = 76.1 ± 2.3 nm.
A similar approach yielded for the height of the lines: R^2 = 0.9916, x_0 = 4.49 ± 0.01 nm, and w = 0.80 ± 0.03 nm.

Scanning Tunneling Microscopy.
STM measurements were carried out in the constant current mode using a home-built low-current STM. The HOPG surface was freshly cleaved and the STM tips were mechanically cut from a Pt:Ir (80:20) wire. A drop of a solution of 1 in 1-phenyl-octane/chloroform (1:19 V/V) was brought onto the surface. The raw data were processed by the application of background filtering. The piezo was calibrated by lowering the bias voltage to 100mV and
raising the tunneling current to 50 pA, which allowed the imaging of the HOPG surface underneath the molecules.

**Optical Microscopy.**
A solution of 1 in chloroform was placed on a glass surface and the instantaneous evaporation was followed with an optical polarization microscope. The images were recorded with a Nikon Eclips ME 600 camera.

**Confocal Fluorescence Microscopy.**
Laser light (COHERENT 411nm, 25mWatt) was coupled into a single-mode optical fiber, reflected by a dichroic beamsplitter (Chroma, 425dcox) and focussed on the sample by a 100x objective (Zeiss, NA = 0.9 ), which was mounted on a Karl Zeiss Axiovert 200 inverted microscope.

Fluorescent light emerging from the focal volume was collected by the same objective, passed through the beamsplitter, filtered (Chroma, HQ435lp), guided through a 50 micron pinhole and finally focussed on a avalanche photo diode (PerkinElmer SPCM-AQR-14) which was coupled to a National Instruments PCI-6036E data acquisition card operating at 20 MHz. The sample was mounted onto a Physik Instrumente P-517.2 CL nanopositioner; sample movement (raster scanning and positioning) and data collection were controlled by a LabView program. Fluorescence spectra were recorded by guiding the emitted light through a fiber optical cable into an Acton SP300I spectrograph.

**Optical Second Harmonic Generation measurements**
The SHG technique is described in details elsewhere (1). For the SHG measurements, a pulsed laser beam from a Ti–sapphire laser (76 MHz×100 fs pulses) with a wavelength of 800 nm was focused onto a 100µm spot at the sample and the outgoing SHG signal was detected after proper filtering with a photomultiplier. The sample was rotated in between two polarizers and rotational anisotropy patterns were measured on different spots of the sample.

The LC cells were made from optical glass, coated with indium-tin oxide (ITO) and untreated polyimide and the other was made from optical glass with on one place a droplet of solvent with molecular wires. Using spacers the cell was adjusted to 6 µm thickness. The cells were filled with 5CB nematic LC molecules, in the isotropic phase, in order to avoid flow alignment.
Supporting figures

Supporting figure S1. STM image (scan size = 21 x 24 nm²) of a self-assembled monolayer of 1 at the interface of HOPG and 1-phenyloctane, $V_{\text{bias}} = -369$ mV, $I_{\text{set}} = 1.0$ pA. The observed distance between two columnar stacks is $3.1 \pm 0.2$ nm, and the distance between two molecules within a stack is $0.8 \pm 0.2$ nm. Both distances are, within experimental error, in agreement with the calculated dimensions of the aromatic part of the molecule (distance between two adjacent molecules = 0.6 nm, diameter = 3.3 nm, see Fig. S4). The computer generated image (Fig. 1D) shows a small rotation of approximately 6 degrees between two neighbouring porphyrin moieties in a stack, which is in good agreement with the STM image. Probably due to their conformational flexibility, the alkyl chains are not resolved. Some of the aliphatic chains are expected to adsorb on the HOPG surface, a number will interdigitate with chains from a neighbouring stack and probably also some will be dangling into the subphase.
Supporting figure S2. Optical microscopy image of a dropcasted solution of 1 in chloroform (concentration = 4.8x10^{-5} M) during the evaporation process on glass. The dark blue part is the glass substrate covered with solution. The whitish lines are porphyrin aggregates that have already been deposited on the dewetted glass surface (the light blue background) upon several pinned retractions of the droplet. The image also shows that aggregates (indicated by the yellow arrows) are already present within the solution, before the retraction of the solvent front.
Supporting figure S3. Optical microscopy image of the spontaneously self-assembled pattern after evaporation of a droplet of 1 in chloroform on a mica surface, highlighting the very large dimensions of the lines. Note that epitaxy does not have a mayor influence, as can be seen from the curvature of the lines. The white spots in the background are caused by the supporting iron layer underneath the mica.
Supporting figure S4. Computer generated image of a stack of 3 molecules of 1. The intermolecular distance indicated in the image was calculated to be 0.6 nm and the diameter of the aromatic part 3.3 nm. The alkyl chains have been omitted for clarity.

Supporting reference