Electronic Supporting Information

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1. Experimental

a. Synthesis.

All chemicals for the synthesis and purification of alkylated isophthalic acids were purchased from Acros Organics, J&K Scientific, TCI Europe, Merck, and Fluorochem, and used without purification. NMR spectra were recorded on a Bruker 400 AV 400 MHz instrument (*Bruker*, *Biospin*) using CDCl$_3$ as the solvent. Chemical shifts (δ) were reported in ppm, referenced to the signal of tetramethylsilane (TMS, 0 ppm). Fourier transform infrared spectra were recorded with a resolution of 2 cm^{-1} on a Bruker Vertex 70 spectrometer in ATR mode (Bruker Platinum ATR module). Melting points were determined using a Reichert Thermovar apparatus and are uncorrected.

Synthesis procedure for DMBs

General procedure. 3,5-Dimethylphenol (150 mg, 1.23 mmol, 1 eq) and potassium carbonate (K$_2$CO$_3$, 204 mg, 1.47 mmol, 1.2 eq) were dissolved in dry dimethylformamide (DMF, 12 mL) and stirred for 1 h at 80 °C. Alkyl bromide (1 eq) was added and the mixture was stirred overnight. Upon reaction completion (as monitored by thin-layer chromatography), the reaction mixture was cooled to room temperature, and DMF was evaporated in vacuo. Water was added to the residue, and the mixture was extracted with dichloromethane (DCM, 3 x 15 mL). Combined organic phases were washed with brine then dried over magnesium sulfate (MgSO$_4$). The solvent was removed in vacuo, and recrystallization from EtOH yielded the pure product.

1-(Octadecyloxy)-3,5-dimethylbenzene. The title compound was prepared using 1-bromooctadecane (409 mg, 1.23 mmol) and isolated as white crystals in 70% yield (320 mg, 0.85 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 6.58 (s, 1H), 6.53 (s, 2H), 3.91 (t, J = 6.6 Hz, 2H), 2.28 (s, 6H), 1.82 – 1.70 (m, 2H), 1.50 – 1.40 (m, 2H), 1.39 – 1.19 (m, 28H), 0.97 – 0.80 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 159.2, 139.1, 122.2, 112.3, 67.8, 31.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.4, 26.1, 22.7, 21.4, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 2915, 2851, 1595, 1472, 1400, 1323, 1297, 1173, 1153, 1068, 865, 844, 829, 821, 716, 685, 643, 584. m.p. 39 °C.
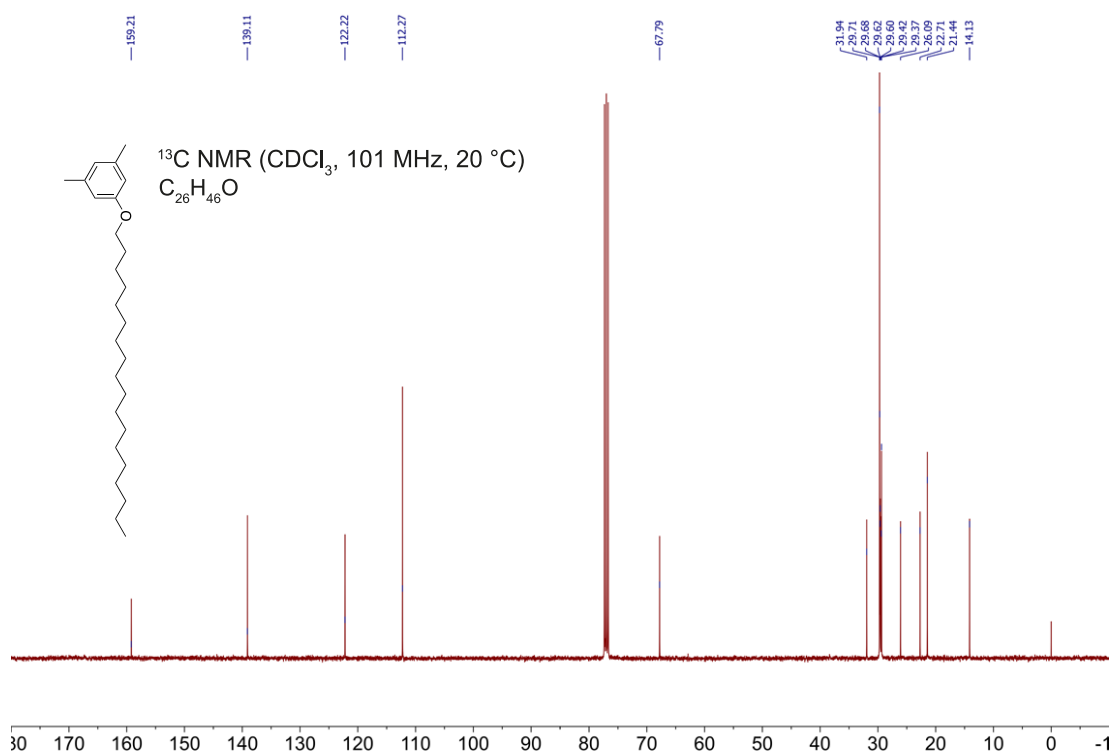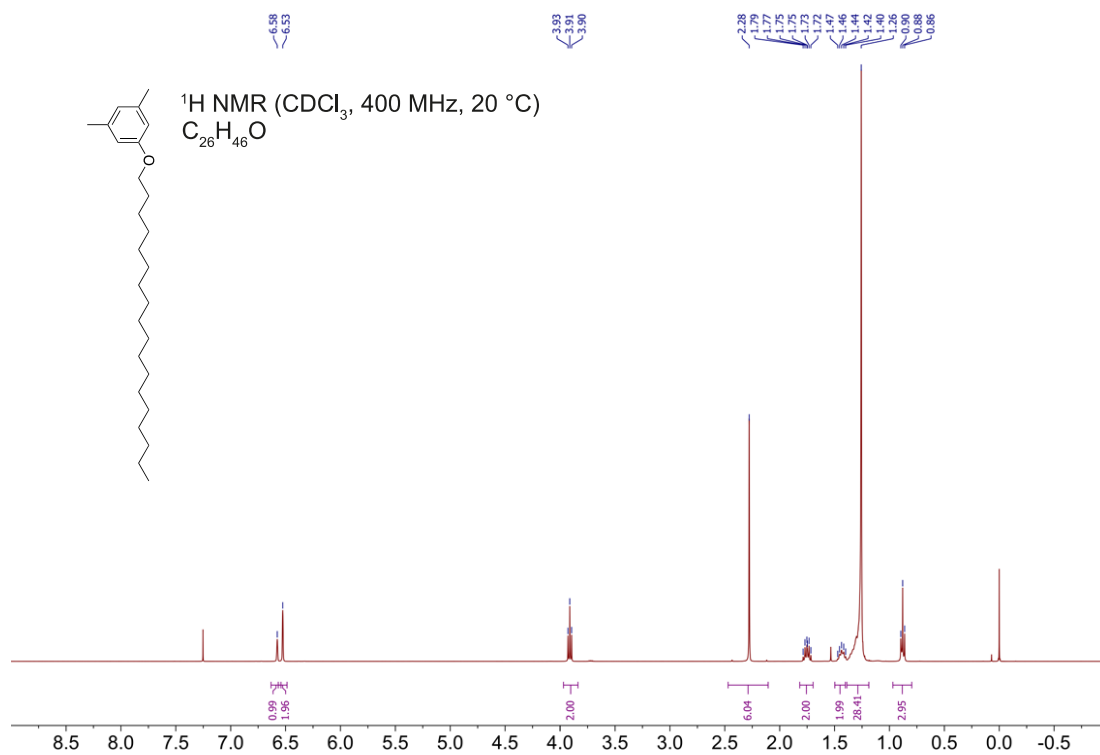
1-(Docosyloxy)-3,5-dimethylbenzene. The title compound was prepared using 1-bromodocosane (478 mg, 1.23 mmol) and isolated as white crystals in 78% yield (414 mg, 0.96 mmol).
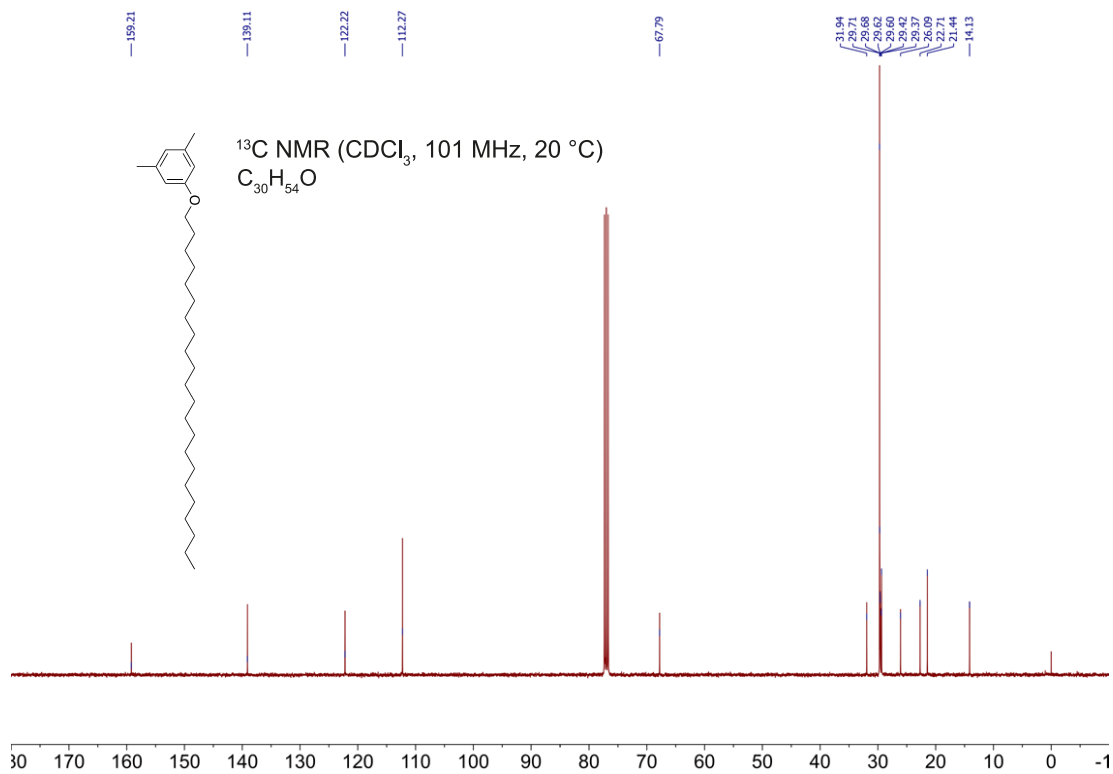
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 6.58 (s, 1H), 6.53 (s, 2H), 3.91 (t, *J* = 6.6 Hz, 2H), 2.28 (s, 6H), 1.82 – 1.69 (m, 2H), 1.50 – 1.40 (m, 2H), 1.36 – 1.21 (m, 36H), 0.96 – 0.83 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 159.2, 139.1, 122.2, 112.3, 67.8, 31.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.4, 26.1, 22.7, 21.4, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 1594, 1472, 1400, 1322, 1296, 1172, 1153, 1067, 955, 864, 842, 826, 716, 685, 643, 584. m.p. 53 °C.

b. Scanning Tunnelling Microscopy

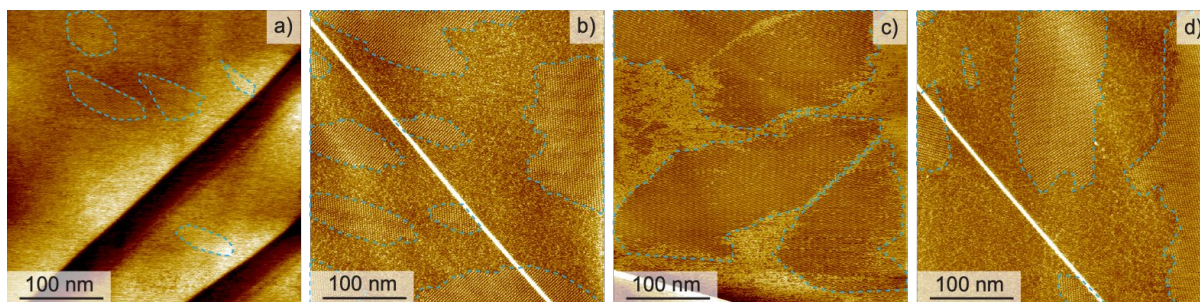All experiments were performed at room temperature (22 – 23 ºC) using a PicoLE (Keysight) STM system operating in constant-current mode at the heptanoic acid/HOPG interface with the tip immersed in the supernatant liquid. In all STM experiments, a freshly cleaved HOPG surface was affixed with a polytetrafluoroethylene (PTFE) solution cell (V = 40-50 μL). STM tips were prepared by mechanical cutting of Pt/Ir wire (80% / 20%, diameter 0.25 mm). Substrates consisted of HOPG (grade ZYB, Advanced Ceramics Inc., Cleveland, OH). Heptanoic acid (HA, Sigma-Aldrich, 98%) was purified by vacuum distillation prior to use (bp 140-142 ºC at 100 mbar). Imaging parameters are indicated in the figure captions and are denoted by V_s for the sample bias and I_t for the tunnelling current. After verifying the quality of the STM tip by obtaining the underlying graphitic lattice (I_t = 200 pA, V_s = − 0.001 V), the sample was allowed to equilibrate for at least 30 minutes before imaging. STM image analysis was carried out using Gwyddion v2.55 (Czech Metrology Institute, Brno, CZ) and SPIP (Image Metrology A/S, Lyngby, DK). Molecular coverages were systematically evaluated based on a set of ~55 large-scale STM images (350 × 350 nm^2) covering a total surface area of ~7.0 μm^2. Each sample was measured in duplicate. Overlap between neighbouring images was excluded by leaving a gap between consecutive images. Molecular coverage analysis was performed on the current STM image, and the coverage was assessed using the masking feature of the image processing software Gwyddion according to the previously published protocol.[38]

2. NMR spectra

^{1}H NMR (CDCl$_3$, 400 MHz, 20 °C)
C$_{26}$H$_{46}$O

6.58, 6.53, 3.93, 3.91, 3.90, 2.28, 1.79, 1.77, 1.75, 1.73, 1.72, 1.47, 1.46, 1.44, 1.42, 1.40, 1.26, 0.90, 0.88, 0.86

0.99 1.96 2.00 6.04 2.00 1.99 28.41 2.95

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

^{13}C NMR (CDCl$_3$, 101 MHz, 20 °C)
C$_{26}$H$_{46}$O

159.21, 139.11, 122.22, 112.27, 67.79, 31.94, 29.71, 29.68, 29.62, 29.60, 29.42, 29.37, 26.09, 22.71, 21.44, 14.13

80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

¹H NMR (CDCl₃, 400 MHz, 20 °C)
C₃₀H₅₄O

6.58
6.53
3.93
3.91
3.90
2.28
1.79
1.77
1.75
1.73
1.72
1.47
1.46
1.44
1.42
1.40
1.26
0.90
0.88
0.86

0.96
1.95
2.00
6.03
2.00
36.49
3.03

¹³C NMR (CDCl₃, 101 MHz, 20 °C)
C₃₀H₅₄O

159.21
139.11
122.22
112.27
67.79
31.94
29.71
29.68
29.62
29.60
29.42
29.37
26.09
22.71
21.44
14.13

3. Additional Scanning Tunnelling Microscopy Images

Figure S1.Large-scale STM images for the self-assembly of the DMBOC18 molecule at the heptanoic acid/HOPG interface showing the formation of smaller, island-type domains. Images were obtained from different samples, at room temperature (22 - 23 °C). Imaging parameters: $V_{bias} = -0.800$ V, $I_{set} = 80 - 100$ pA. For the sake of clarity, domains are circled in blue.
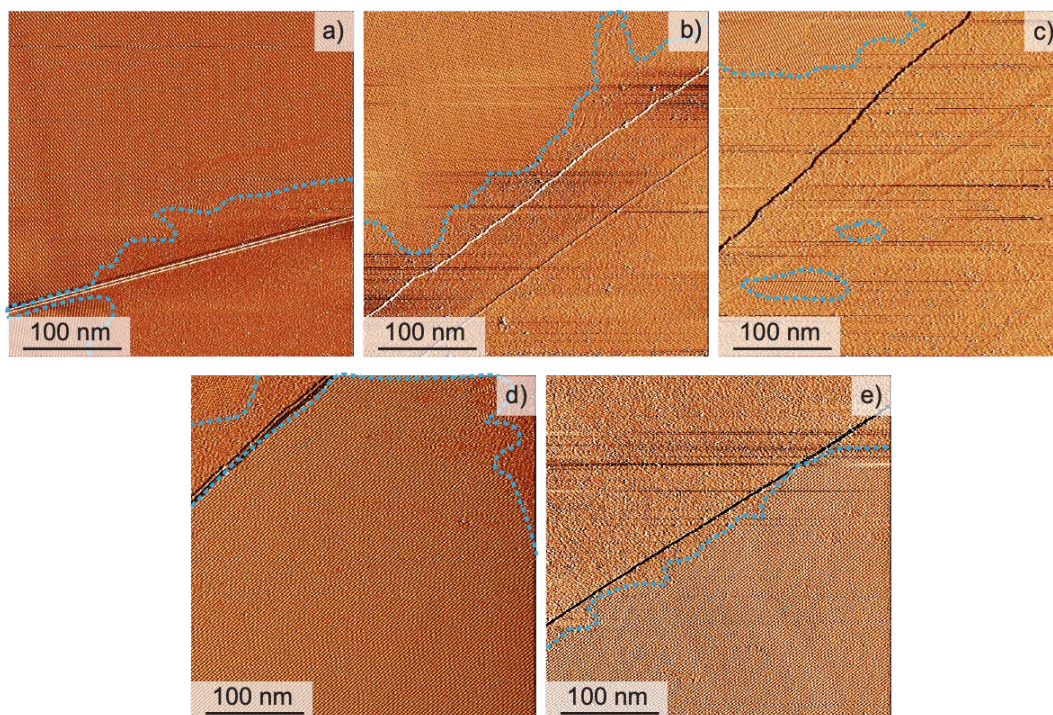
Figure S2. Large-scale current STM images for the self-assembly of DMBOC18 at the heptanoic acid/HOPG interface showing the impact of the HOPG terraces on the assembly. Images were obtained from different samples, at room temperature (22 - 23 °C). Imaging parameters: $V_{bias} = -0.800$ V, $I_{set} = 80 - 100$ pA.

4. STM data analysis

Table S1. Unit-cell parameters for the sub-assemblies formed by DMBOC18 molecules at the heptanoic acid/HOPG interface.

| DMBOC18	$a \pm$ SD (nm)	$b \pm$ SD (nm)	$\gamma \pm$ SD (deg)
4-subassembly	1.04 ± 0.08	3.58 ± 0.05	89 ± 2
6-subassembly	1.0 ± 0.1	3.6 ± 0.1	89 ± 2

Table S2. Adsorption parameters for DMBOC18 at the heptanoic acid/HOPG interface based on Langmuir, Hill and Matsuda model regression fitting at 25 °C. K_L, K_H, n, σ and K_e are parameters of the fit, while K_n, ΔG_{SAM}, ΔG_n and ΔG_e are calculated values.

Langmuir	$K_L \pm$ SD / mol dm^{-3}	$\Delta G_{SAM} \pm$ SD / kJ mol^{-1}	r^2			
	$(2.30 \pm 0.05) \times 10^{-3}$	-15.01 ± 0.1	0.640			

Matsuda	K_e / mol dm^{-3}	σ	$K_n \pm$ SD / mol dm^{-3}	$\Delta G_e \pm$ SD / kJ mol^{-1}	$\Delta G_n \pm$ SD / kJ mol^{-1}	r^2
	230 ± 41	0.2 ± 0.2	46 ± 50	-13.5 ± 0.4	-9 ± 2	0.847

Hill	K_H / mol dm^{-3}	n	ΔG_{SAM} / kJ mol^{-1}	r^2	MC error analysis	
					$n \pm$ SD	$\log K \pm$ SD
	$(2.34 \pm 0.05) \times 10^{-3}$	7.1 ± 0.8	-15.0 ± 0.1	0.998	7 ± 2	2.37 ± 0.01

5. Details of data and error analysis
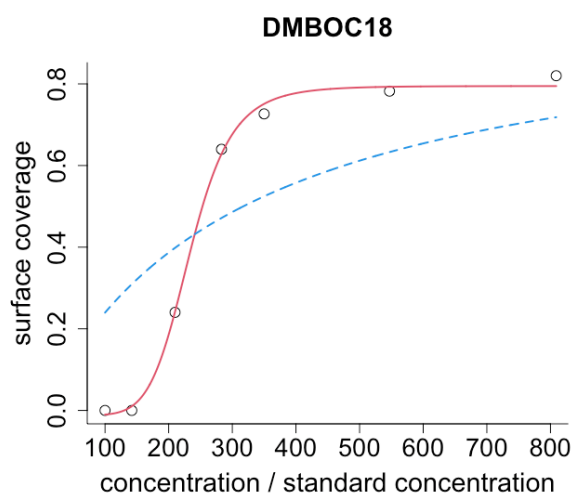
Figure S3. Surface coverage analysis for self-assembly of DMBOC18 at heptanoic acid/HOPG interface at room temperature (22 °C) using Hill adsorption model (—) and Langmuir adsorption model (⋯). The standard concentration used was $c° = 1 \times 10^{-5}$ mol dm^{-3}.
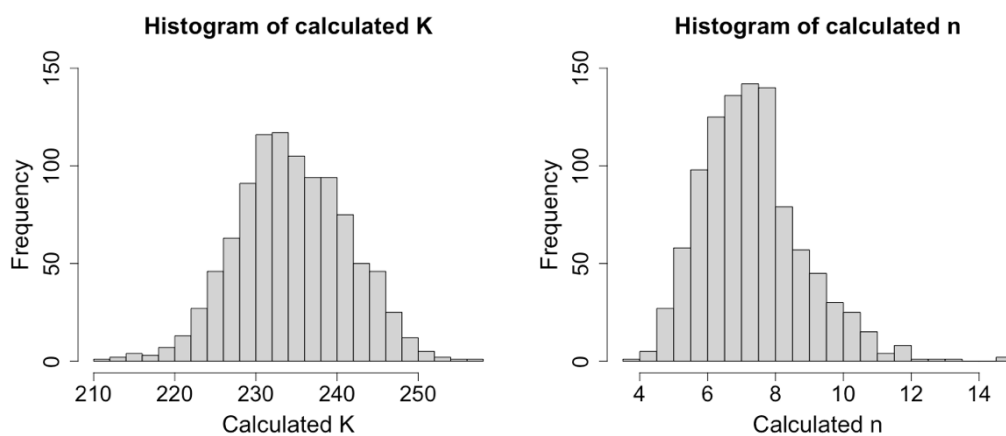
Figure S4. Monte Carlo numerical error analysis of Hill fitting parameters for DMBOC18. The histograms represent the distribution of 1000 simulations.
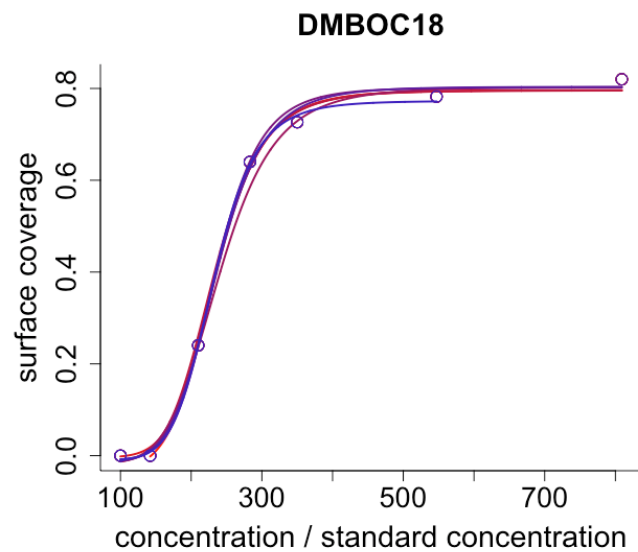
Testing the dependence of a Hill fit on the sensitivity to the inclusion of data points
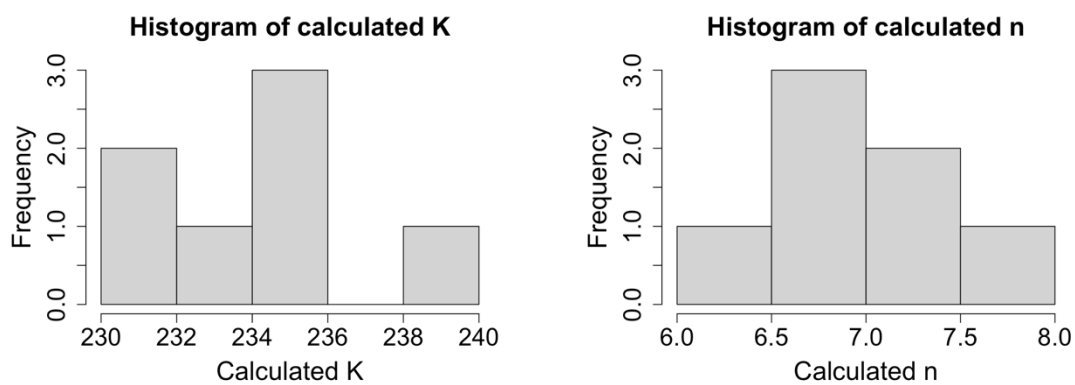
The robustness of the parameters of the best fit to the Hill model has been tested by taking the original data set (concentration vs. coverage) from it creating a series of new data sets. Each new dataset has one of the points from the original data set missing. New data sets were subjected to the same fitting procedure as the original data sets. Obtained parameters of the fit in each modified data set were collected as a matrix, and the values of those parameters are presented as a histogram (Figure S4). The mean value of both fitting parameters is presented in Table S3 together with the standard deviation. The standard deviation, in this case, can be taken as a measure of the sensitivity of the value of fitting parameters to the inclusion of data points in the analysis. As expected, the points that have the strongest influence on the values of fitting parameters are those that correspond to partial surface coverage.

Table S3. Error analysis of the data point sensitivity for analysis using the Hill adsorption model.

| molecule	$n \pm \mathrm{SD}$	$10^5 \, (K \pm \mathrm{SD}) \, / \, \mathrm{mol} \, \mathrm{dm}^{-3}$
DMBOC18	7.0 ± 0.5	234 ± 3

Figure S5. Dependence of Hill fit to data points included in the data set for DMBOC18.


Figure S6. Histograms of parameters *n* and *K* in the Hill model when testing the robustness of the model by removing a single data point from the set in the case of DMBOC18.

6. Details of 2D Ising model for molecular self-assembly on surfaces

In addition to optimising parameters discussed in the main text, to minimize finite-size effects when modelling bulk systems, the grid size should be optimised (Figure S7). Considering the computational costs and efficiency as well as the accuracy of the calculations, the grid size of 20 × 20 was chosen as an optimum for the analysis of experimental data by the regression fitting using the 2D Ising model.
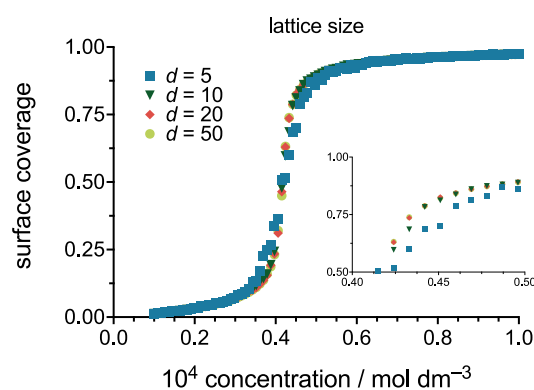
Figure S7. Coverage vs. concentration curves obtained by Monte Carlo simulations of the 2D Ising model adopted for self-assembly on surfaces as a function of the lattice size ($T = 298.15$ K, $\mu^0 = -25$ kJ mol^{-1}, $J = 3.8$ kJ mol^{-1}). All the simulations were produced using the same number of equilibration and production MC sweeps ($N_{eq} = 10000$, $N_{prod} = 8000$).
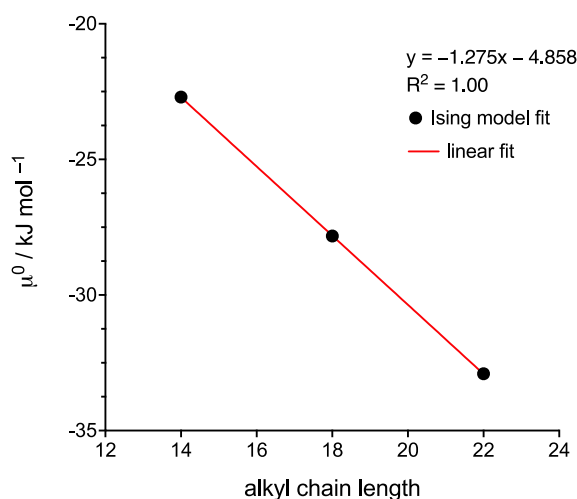
Figure S8. Gibbs free energy for a molecule binding to the surface ($\mu^\ominus$), as defined by a modified 2D Ising model, dependence on alkyl chain length for ISA derivatives at 25 °C. The solid line denotes the best-fitting line obtained by linear regression.