Supporting Information

Design and STM investigation of intramolecular folding in self-assembled monolayers on surface.

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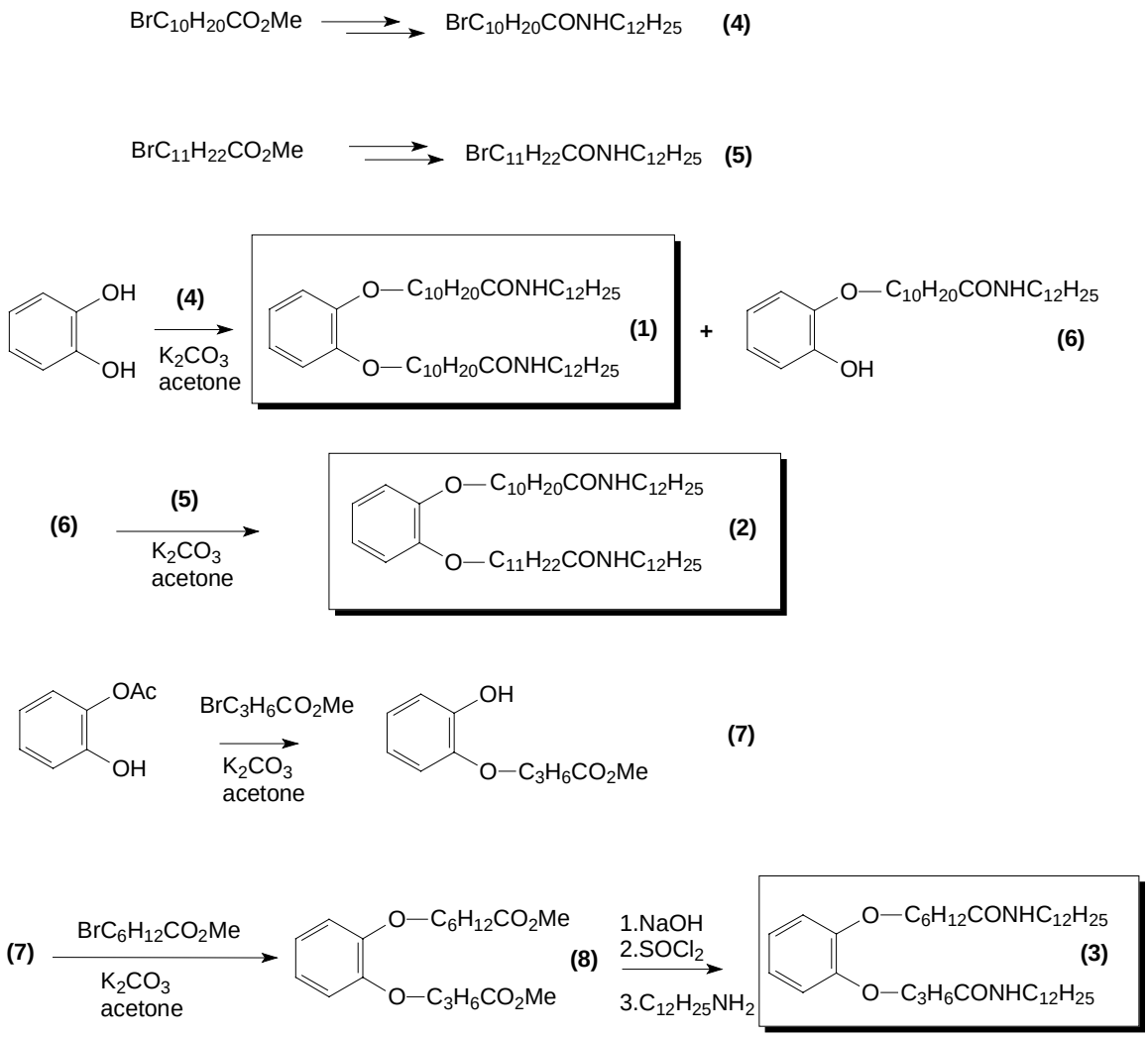
Synthesis and characterization.



11-Bromo-undecanoic acid dodecylamide (4)

Thionylchloride (0.7 ml, 1.1 g, 1.2 equiv.) was added drop-wise to a stirred solution of 11-bromo-undecanoic acid (2.0 g, 7.5 mmol) in CH_2Cl_2 (50 ml). After addition was complete the reaction mixture was refluxed for 2h, cooled to RT, and concentrated in vacuum to remove excess thionylchloride. The acid chloride (2.0 g) was dissolved in CH_2Cl_2 (50 ml) and dodecylamine (1.5 g, 8 mmol) and Et_3N (0.9 g, 9 mmol) were slowly added. After addition was complete the reaction mixture was refluxed for 12h, cooled to RT, washed ($NaHCO_3$ (aq. sat), H_2O; 2 x 50 ml), dried over Na_2SO_4, filtered over silica and concentrated in vacuum to give a white powder. Yield 2.4 g (5.6 mmol, 75 %); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.42 (br, 1H), δ 3.37 (t,^{3}J=7.0, 2H), δ 3.20 (q, J=7.3, 2H), δ 2.12 (t, ^{3}J=7.7, 2H), δ 1.81 (qn, ^{3}J=7.3, 2H), δ 1.58 (t, ^{3}J=6.9 1H), δ 1.45 (m, 2H), δ 1.22 (m, 36H), δ 0.85 (t, ^{3}J=6.6, 3H).^{13}C- NMR (400 MHz, $CDCl_3$): δ 173.3, 39.8, 37.2, 34.4, 33.1, 32.2, 31.2, 30.0, 29.9, 29.9, 29.8, 29.8, 29.6, 29.5, 29.0, 28.4, 27.2, 26.1, 23.0, 14.4.

12-Bromo-dodecanoic acid dodecylamine (5)

This compound was synthesized as described above for **4**, starting from 12-bromo-dodecanoic acid (2.0 g). Yield 2.2 g (4.9 mmol, 70%) of a white powder. ^{1}H- NMR (400 MHz, $CDCl_3$): δ 5.37 (br, 1H), δ 3.38 (t,^{3}J=7.0, 2H), δ 3.21 (q, J=7.3, 2H), δ 2.12 (t, ^{3}J=7.7, 2H), δ 1.83 (qn, ^{3}J=7.3, 2H), δ 1.59 (t, ^{3}J=6.9 1H), δ 1.44 (m, 2H), δ 1.39 (t, ^{3}J=6.8 1H) δ 1.22 (m, 36H), δ 0.85 (t, ^{3}J=6.6, 3H).^{13}C- NMR (400 MHz, $CDCl_3$): δ 173.0, 39.5, 36.9, 34.0, 32.8, 31.9, 30.9, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.4, 29.4, 29.3, 28.7, 28.1, 26.9, 25.8, 22.7, 14.1.

11-[2-(10-Dodecylcarbamoyl-decyloxy)-phenoxy]-undecanoic acid dodecylamide (1)

Potassium carbonate (0.5 g, 3.6 mmol) was added to a solution of catechol (0.04 g, 0.36 mmol) in acetone (40 ml) under an atmosphere of N_2, After refluxing the suspension for 10 min, 11-bromo-undecanoic acid dodecylamide **4** (0.4 g, 0.9 mmol) was added and refluxing was continued for 48 h. The mixture was filtered, the residue of the filtration was collected and resuspended in $CHCl_3$. This suspension was filtered again, and the filtrates were collected and concentrated in vacuo. The oily remains were supended in MeOH (10 ml) from which the product precipitated as a white powder that was collected on a filter and dried under vacuum. Yield 150 mg (0.18 mmol, 50 %); mp.115-116˚; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.86 (s, 4H), δ 5.45 (br, 2H), δ 3.96 (t, ^{3}J=6.6, 4H), δ 3.21 (q, J=6.8, 4H), δ 2.12 (t, ^{3}J=7.1, 4H), δ 1.77 (m, 4H), δ 1.59 (m, 4H), δ 1.44 (m, 4H), δ 1.23 (m, 72H), δ 0.84 (t, ^{3}J=6.6, 6H). ^{13}C- NMR (400 MHz, $CDCl_3$): δ 173.0, 149.2, 120.9, 114.0, 69.2, 39.5, 36.9, 31.9, 29.7, 29.6, 29.6, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 26.9, 26.1, 25.9, 22.7, 14.1. EI-MS: m/z 812, 586, 474.

11-(2-Hydroxy-phenoxy)-undecanoic acid dodecylamide (6)

Potassium carbonate (0.2 g, 1.4 mmol) was added to a solution of catechol (0.13 g, 1.2 mmol) in acetone (40 ml) under an atmosphere of N_2, After refluxing the suspension for 10 min, 11-bromo-undecanoic acid dodecylamide **4** (0.5 g, 1.1 mmol) was added and refluxing was continued for 48 h. The salts were removed by filtration and the filtrate was concentrated vacuum. The oily residue was purified by column chromatography (silica,

eluent pentane-EtOAc 50/50) to give the product as a colorless oil. Yield 300 mg (0.65 mmol, 55%); ^{1}H- NMR (400 MHz, $CDCl_3$): δ 6.76-6.94 (m, 4H), δ 5.69 (s, 1H), δ 5.42 (br, 1H), δ 4.03 (t, ^{3}J=6.6, 2H), δ 3.24 (q, J=6.8, 2H), δ 2.16 (t, ^{3}J=7.1 2H), δ 1.80 (t, ^{3}J=7.6, 2H), δ 1.45 (m, 2H) δ 1.25 (m, 36H), δ 0.84 (t, ^{3}J=6.6, 3H). ^{13}C- NMR (400 MHz, $CDCl_3$): δ 172.8, 145.5, 120.9, 119.7, 114.1, 111.3, 68.5, 39.2, 36.5, 31.6, 29.3, 29.3, 29.2, 29.2, 29.1, 29.0, 28.9, 28.9, 28.8, 26.6, 25.7, 25.5, 22.4, 13.8.

12-[2-(10-Dodecylcarbamoyl-decyloxy)-phenoxy]-dodecanoic acid dodecylamide (2)

Potassium carbonate (0.1 g, 0.7 mmol) was added to a solution of **6** (80 mg, 0.27 mmol) in acetone (30 ml) under an atmphere of N_2, After refluxing the suspension for 10 min, the 12-bromo-dodecanoic acid dodecylamine **5** (0.12 g, 0.27 mmol) was added and refluxing was continued for 5 days. The salts were removed by filtration, and washed with $CHCl_3$. The filtrates were combined, concentrated in vacuum to give a yellow oil. Upon stirring of this oil in MeOH (10 ml), the product precipitated as white powder that was collected on a filter and dried under vacuum. Yield 100 mg (0.12 mmol, 67%). mp. 114-115°; ^{1}H- NMR (400 MHz, $CDCl_3$): δ 6.83 (s, 4H), δ 5.46 (br, 2H), δ 3.93 (t, ^{3}J=6.6, 4H), δ 3.18 (q, J=6.8, 4H), δ 2.09 (t, ^{3}J=7.1, 4H), δ 1.75 (m, 4H), δ 1.52 (m, 4H), δ 1.40 (m, 4H), δ 1.20 (m, 72H), δ 0.82 (t, ^{3}J=6.6, 6H). ^{13}C- NMR (400 MHz, $CDCl_3$): δ 173.5, 149.7, 121.4, 118.9, 114.6, 69.7, 39.9, 37.3, 32.3, 30.1, 30.0, 30.0, 29.9, 29.9, 29.9, 29.8, 29.7, 27.4, 26.5, 26.3, 25.9, 23.1, 14.5. EI-MS: m/z 826, 600, 474.

7-(2-Hydroxy-phenoxy)-heptanoic acid methyl ester (7)

This compound was prepared as described above for **6**, starting from acetic acid 2-hydroxy-phenylester (= mono acetyl catechol)[1] (1.2 g, 8 mmol), potassium carbonate (1.4 g, 10 mmol), and 7-bromoheptanoic acid methylester[2] (1.8 g, 8 mmol). The crude product was purified by column chromatography (silica, eluent 1 % MeOH in $CHCl_3$) to give a yellow oil that solidified on standing. Yield 1.1 g (4.3 mmol, 54 %); ^{1}H- NMR (400 MHz, $CDCl_3$): δ 6.75-6.85 (m, 4H), δ 5.77 (s, 1H), δ 3.95 (t, ^{3}J=6.6, 2H), δ 3.61 (s, 3H), δ 2.26 (t, ^{3}J=7.3, 2H), δ 1.75 (t, ^{3}J=7.0 , 2H), δ 1.60 (t, ^{3}J=7.1, 2H), δ 1.43 (m, 2H), δ 1.32 (m, 2H); ^{13}C- NMR (400 MHz, $CDCl_3$): δ 175.0, 143.7, 118.5, 117.1, 112.4, 109.9, 66.1, 48.8, 31.2, 26.4, 26.1, 23.0, 22.1; EI-MS: m/z 252, 220, 110.

7-[2-(3-Methoxycarbonyl-propoxy-phenoxy]-heptanoic acid methyl ester (8)

This compound was prepared as described above for **2**, starting from **9**, (1.0 g, 3.9 mmol), potassium carbonate (1.4 g, 10 mmol), and 3-bromobutyric acid methylester[3] (0.9 g, 5 mmol), to give an oil, which was used in the next step without further purification. Yield 0.7 g (2 mmol, 52 %); ^{1}H- NMR (400 MHz, $CDCl_3$): δ 6.86 (s, 4H), δ 4.01 (t, ^{3}J=6.2, 2H), , δ 3.95 (t, ^{3}J=6.6, 2H), δ 3.66 (s, 3H), δ 3.65 (s, 3H), δ 2.54 (t, ^{3}J=7.3, 2H), δ 2.30 (t, ^{3}J=7.0 , 2H), δ 2.12 (t, ^{3}J=7.1, 2H), δ 1.79 (t,^{3}J=7.0, 2H), δ 1.64 (m, 2H), δ 1.47 (m, 2H), δ 1.38 (m, 2H); ^{13}C- NMR (400 MHz, $CDCl_3$): δ 173.4, 172.9, 148.6, 148.2, 120.8, 120.5, 113.9, 113.3, 68.3, 67.4, 50.8, 50.7, 33.3, 29.8, 28.5, 28.2, 25.1, 24.2, 24.1.

7-[2-(3-Dodecylcarbamoyl-propoxy)-phenoxy]-heptanoic acid dodecylamide (3)

Compound **10** (0.35 g, 1 mmol) was saponified by dissolution in NaOH (2.5 M) in water/ethanol 1/1, followed by refluxing for 2h. The mixture was left to stand for 12 h, poured into NaCl (aq, sat. 50 ml) and washed with EtOAc (50 mL). The aqueous layer was acidified to pH 2 and extracted again with EtOAc (2 x 50 ml) The organic layer was dried over Na_2SO_4, concentrated in vacuum to give a dark oil. ^{1}H NMR indicated that saponification of the ester groups was complete. The crude product was dissolved in CH_2Cl_2 (10 ml) and thionylchloride (300 µl, 500 mg) was added. The reaction mixture was refluxed for 2 h, and concentrated in vacuum to remove excess thionylchloride. The oily residue was dissolved in CH_2Cl_2 (10 ml) and dodecylamine (600 mg, 3.2 mmol) and Et_3N (350 mg, 3,5 mmol) were added. The reaction mixture was refluxed 12 h and concentrated in vacuum to give the crude product that was purified by column chromatography (silica, eluent 2% MeOH in $CHCl_3$). Yield 0.2 g (0.3 mmol, 30 % over 3 steps) of a white solid; mp. 94-96˚; ^{1}H- NMR (400 MHz, $CDCl_3$): δ 6.85 (s, 4H), δ 6.02 (br, 1H), δ 5.64 (br, 1H), δ 3.99 (t, ^{3}J=6.2, 2H), δ 3.95 (t, ^{3}J=6.6, 2H), δ 3.16 (m, 4H), δ 2.38 (t, ^{3}J=7.3, 2H), δ 2.12 (m, 4H), δ 1.76 (t, ^{3}J=7.0 , 2H), δ 1.62 (t, ^{3}J=7.7, 2H), δ 1.20-1.47 (m, 44H), δ 0.83 (t, ^{3}J=7.0, 6H); ^{13}C- NMR (400 MHz, $CDCl_3$): δ 173.2, 172.8, 149.3, 148.9, 121.7, 121.4, 114.7, 114.0, 69.1, 68.4, 39.9, 39.8, 36.8, 33.3, 32.2, 29.9, 29.9, 29.9, 29.9,, 29.8, 29.6, 29.5, 29.4, 29.2, 27.3, 26.1, 25.9, 25.7, 23.0, 14.4. EI-MS: m/z 658, 405, 254.

Molecular Modelling.

Molecular modeling calculations were carried out using the compass forcefield, as implemented in Materials Studio, a product of Accelrys, San Diego, Ca, USA. The energy minimizations were carried out in the gas phase with a dielectric constant of 1. All energy-terms were included with the exception of an explicit hydrogen-bonding term. For the non-bonding interactions a cut-off radius of 12.5 Å was used, with a spline width of 3 Å, and a buffer width of 1.0 Å. A graphite, sheet 20 x 30 atoms in size, with fixed cartesian position for the carbon atoms was used as the substrate. All structures were subjected to energy minimization using the Fletcher-Reeves algorithm, to a final gradient with maximum derivative of 0.001 kcal/mol. The folding abilities for the derivatives were expressed by comparison of the total potential energy for the energy-minimized intramolecular H-bonded structure, with the optimized extended conformation without intramolecular hydrogen bond and with all CH_2-CH_2 bonds in trans configuration, and both conformations in close contact with the graphite substrate. No direct comparison between derivatives was made.

STM

STM Experiments were performed using a Discoverer Scanning Tunneling Microscope (Topometrix Inc., Santa Barbara, CA) along with an external pulse/function generator (model HP 8111 A), with negative sample bias. Tips were electrochemically etched from Pt/Ir wire (80%/20%, diameter 0.2 mm) in 2N KOH/ 6N NaCN solution in water. Highly oriented pyrolytic graphite (HOPG, grade ZYB, Advanced Ceramics Inc., Cleveland,

OH) was used as a substrate. The saturated solutions of each compound were prepared in 1-phenyloctane (Aldrich 99%) and 1-octanol (Aldrich 99%) via several heating and cooling cycles. At the 1-phenyloctane – graphite interface, no monolayers were observed. To image the 10,10- and 10,11-spacers, the STM tip, which was dipped once in a saturated solution of 1-octanol, was immersed in the saturated liquid layer at the 1-phenyloctane – graphite interface. STM images were obtained in the constant height mode. This specific procedure was followed because the 1-octanol – graphite interface did not provide stable imaging conditions: though the same monolayer structures were observed, they disappeared fast. For the 3,6-spacers, the measurements were performed at the saturated 1-octanol – graphite interface. STM images were calibrated and analyzed with Scanning Probe Image Processor (SPIP) software (Image Metrology ApS) using images of underlying graphite recorded at the same positions.

References

[1] Olcott et al. *J.Am.Chem.Soc*, **1937,** 59, 392.

[2] This compound was synthesized from the corresponding nitrile according to a literature procedure: Woolford, R.G, *Can.J.Chem*, **1962**, 40, 1846-1850, and esterified as in ref 3.

[3] Miyaoka et al. *Tetrahedron*, **2000,** 56, 41, 8083 – 8094.