

## Nanoscale patterning of solid supported membranes by integrated diffusion barriers

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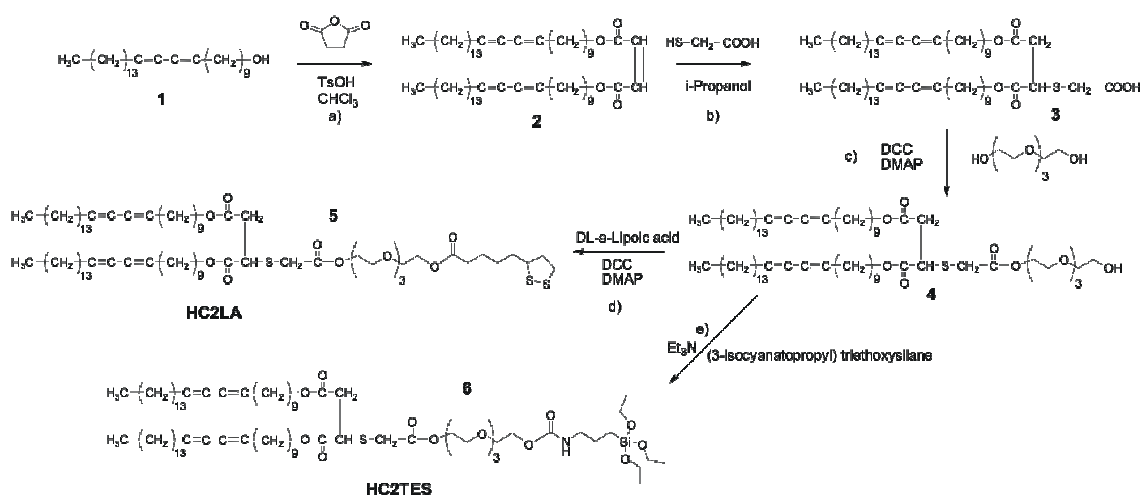
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### Synthetic procedures

All reagents were purchased from commercial sources, mostly from Sigma-Aldrich (Schnelldorf, Germany) and used without further purification. Solvents were purchased from Fischer Scientific (Niderau, Germany) in HPLC grade and the dry solvents from Across Organics (affiliated Fischer Scientific, Niderau, Germany).

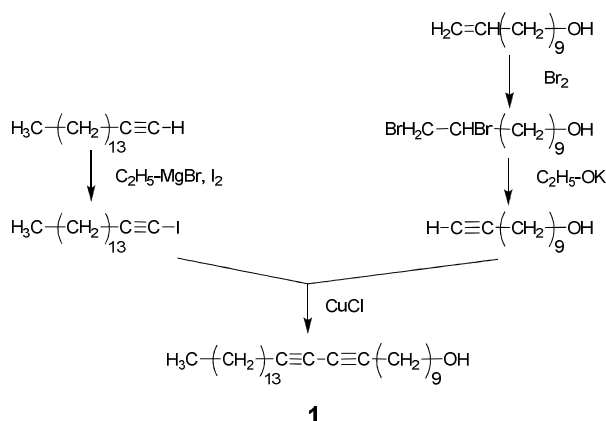
The purification after each reaction was performed by column chromatography, using Acros Organics (Geel, Belgium) silica gel 60A with a positive nitrogen pressure. All reactions were followed by thin layer chromatography (TLC) on Alugram Sil G/UV form Macherey-Nagel (Düren, Germany). The developer used to reveal the presence of molecules on the TLC was a mixture of resorcinol monomethyl ester and sulfuric acid (1:1) in ethanol.

The purity of the obtained products was verified with NMR (Bruker Biospin 250 MHz spectrometer) and mass spectrometry (VG ZAB2-SE-FPD spectrometer from Spectrofield).



Scheme S 1: Synthesis scheme for HC2LA (5) and HC2TES (6)

### Heptacos-10,12-diyne-1-ol (1)



Scheme S 2: Synthesis scheme for Heptacos-10,12-diyne-1-ol (1)

1-iodo-hexadec-1-yn-1-ol can be obtained starting from hexadec-1-yn-1-ol, reacting with ethylmagnesium bromide in diethyl ether, followed by the addition of iodine. Undec-10-yn-1-ol is obtained by the bromination of undec-10-ene-1-ol followed by the elimination with potassium ethanolate in ethanol. The both components were coupled via the Cadiot-Chodkiewicz coupling reaction involving copper (I) ions.<sup>1</sup>

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ [ppm] 3.62 (t, 2H), 2.22 (t, 4H), 1.61 – 1.38 (m, 6H), 1.33 – 1.18 (m, 32H), 0.86 (t, 3H).

### Maleic acid-bis(heptacos-10,12-diyne-1-yl)-ester (2)

<sup>1</sup> B. Tieke, G. Wegner, D. Naegele, H. Ringsdorf, *Angew. Chem.* **1976**, 88, 805; *Angew. Chem. Int. Ed.* **1976**, 15, 764.

20g (51,5mmol) heptacos-10,12-diyne-1-ol (**1**) were added to a solution of 2,4g (25,8mmol) maleic anhydride and 1,3g (7,5mmol) p-toluenesulfonic acid in 150ml dry chloroform. The reaction mixture was heated to reflux 24 hours with a water separator. After completion of the reaction, the mixture was washed once with water, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The product was purified through recrystallisation in acetone and flash chromatography. Eluents: petrol ether/ethyl acetate (95:5). Yield: 14g (58%). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ [ppm] 6.23 (s, 2H), 4.18 (t, 4H), 2.22 (t, 8H), 1.61 – 1.38 (m, 12H), 1.33 – 1.18 (m, 64H), 0.86 (t, 6H).

*Succinic acid-2-thioglycolic acid-1,4-bis(heptacos-10,12-diyne)-ester (**3**)*

0,65g (7,06mmol) thioglycolic acid and 13ml tetramethylethylenediamine were added to a solution of 3g (6,44mmol) of **2** in 50ml dry THF. The reaction mixture was then shortly heated to reflux and subsequently left stirring for two days at room temperature. After completion of the reaction, the solvent was evaporated, the remaining solid dissolved in ethyl acetate and acidified with 2N H<sub>2</sub>SO<sub>4</sub>. The mixture was subsequently washed three times with water, the organic phase dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The product was purified with flash chromatography. Eluents: chloroform/methanol (20:1). Yield: 2g (56%). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ [ppm] 4.18 – 3.92 (m, 4H), 3.90 – 3.75 (dt, 1H), 3.54 – 3.33 (m, 2H), 3.03 – 2.65 (m, 2H), 2.22 (t, 8H), 1.64 – 1.42 (m, 12H), 1.41 – 1.12 (m, 64H), 0.86 (t, 6H).

*Succinic acid-2-(thioglycolic acid-[tetraethylene glycol ester])-1,4-bis(heptacos-10,12-diyne)-ester (**4**)*

In a 100ml one neck round bottomed flask, 0,50g (0,52mmol) of **3** and 110mg (0,52mmol) DCC were dissolved in 25ml dry DCM. The mixture was stirred at room temperature for 30 minutes before the step-wise addition of 1,0g (5,2mmol) of tetraethylene glycol. After another half an hour stirring, ~10mg (0,01mmol) of DMAP was added and the reaction left stirring overnight. The reaction was monitored via TLC. Eluents: hexane/ethyl acetate (1:2); R<sub>f</sub> ≅ 0,40. After completion of the reaction, the mixture was diluted with 150ml DCM and successively washed with a solution of Na<sub>2</sub>CO<sub>3</sub> and water. The organic phase was then dried over MgSO<sub>4</sub> and the solvent evaporated. The purification was done with flash chromatography. Yield: 230mg (40%). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ [ppm] 4.33 – 4.22 (m, 2H), 4.17 – 3.92 (m, 4H), 3.85 – 3.54 (m, 16H), 3.54 – 3.33 (m, 2H), 3.03 – 2.65 (m, 2H), 2.22 (t, 8H), 1.64 – 1.42 (m, 12H), 1.41 – 1.12 (m, 64H), 0.86 (t, 6H).

*Succinic acid-2-(thioglycolic acid-[tetraethylene glycol ester-[D,L- $\alpha$  lipoic acid ester]])-1,4-bis(heptacos-10,12-diynyl)-ester (5)*

Same procedure as for product **4**.

In a 100ml one neck round bottomed flask, 105mg (0,50mmol) of D,L- $\alpha$  lipoic acid and 105mg (0,50mmol) DCC were dissolved in 25ml dry DCM. The mixture was stirred at room temperature for 30 minutes before the step-wise addition of 115mg (0,10mmol) of **4**. After another half an hour stirring, ~10mg (0,01mmol) of DMAP was added and the reaction left stirring overnight. The reaction was monitored via TLC. Eluents: hexane/ethyl acetate (1:2);  $R_f \cong 0,80$ . After completion of the reaction, the mixture was diluted with 150ml DCM and successively washed with a solution of  $\text{Na}_2\text{CO}_3$  and water. The organic phase was then dried over  $\text{MgSO}_4$  and the solvent evaporated. The purification was done with flash chromatography. Yield: 190mg (80%).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  [ppm] 4.32 – 3.99 (m, 8Ha), 3.84 – 3.76 (dd, 1Hb), 3.74 – 3.50 (m, 12Hc), 3.38 (d, 2Hd), 3.13 (dd,  $J = 7.0, 14.3$ , 2He), 2.97 – 2.64 (m, 2Hf), 2.53 – 2.26 (m, 3Hg), 2.22 (t,  $J = 6.8$ , 8Hh), 1.98 – 1.53 (m, 18Hi), 1.54 – 1.09 (m, 66Hj), 0.84 (t, 6Hk).

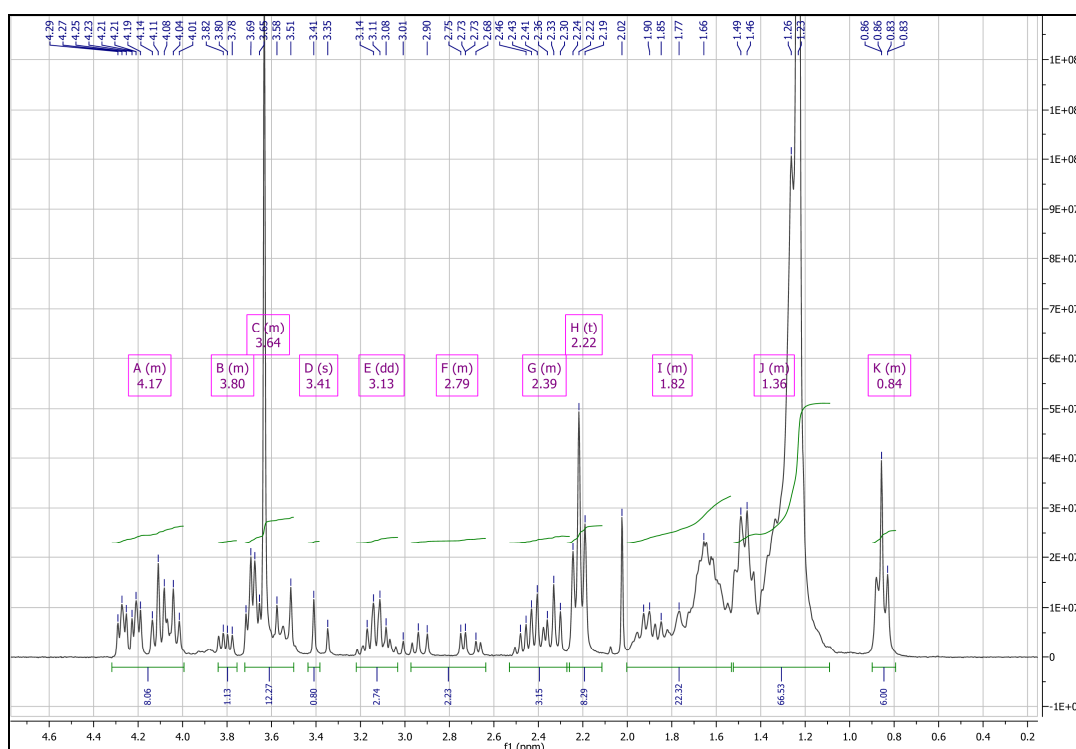


Figure S 1:  $^1\text{H}$ -NMR spectra of HC2LA (**4**)

*Succinic acid-2-(thioglycolic acid-[tetraethylene glycol ester-[3-(triethoxysilyl) propylcarbamate]]-1,4-bis(heptacos-10,12-diynyl)-ester (6):*

In a 50ml three necked round bottomed flask equipped with an argon inlet and a reflux condenser, 115mg (0,10mmol) of **4**, 29mg (0,50mmol) of (3-isocyanatopropyl) triethoxysilane, 3 drops of triethylamine were introduced in 20ml dry THF. The mixture was heated to reflux for 48 hours under argon atmosphere. After completion of the reaction, the mixture was concentrated and purified with flash chromatography. The silica gel used for the chromatography was first passivated 10 minutes with a 5% solution of hexamethyldisilazane in the eluent. Eluents: hexane/ethyl acetate (1:2);  $R_f \cong 0,75$ . Yield: 40mg (30%).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  [ppm] 4.85 (s, 1Ha), 4.30 – 4.15 (m, 2Hb), 4.15 – 4.00 (m, 6Hc), 3.80 (m, 7Hd), 3.73 – 3.59 (m, 12He), 3.59 – 3.33 (m, 2Hf), 3.15 (dd, 2Hg), 3.02 – 2.64 (m, 2Hh), 2.22 (t, 8Hi), 1.71 – 1.38 (m, 14Hj), 1.32 – 1.13 (m, 66Hk), 0.85 (t, 6Hl), 0.67 – 0.54 (m, 2Hm).

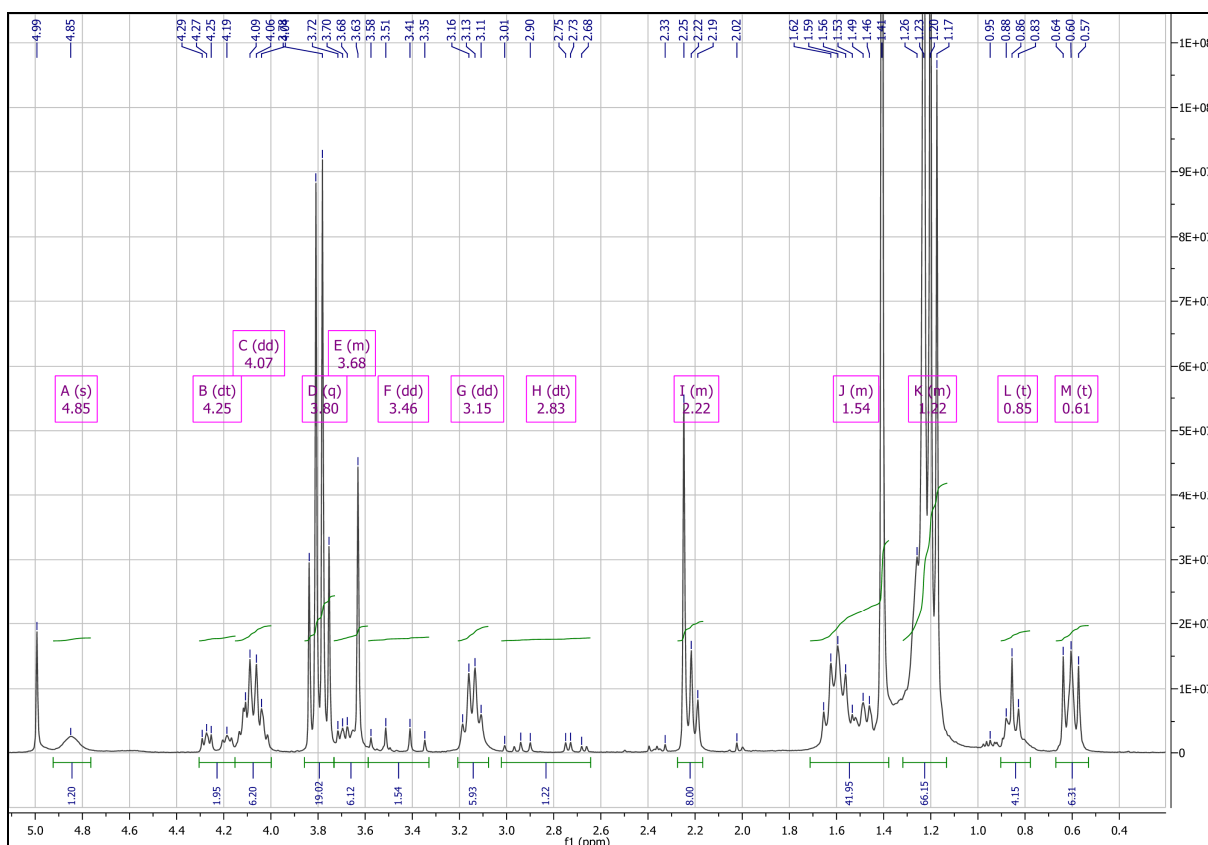
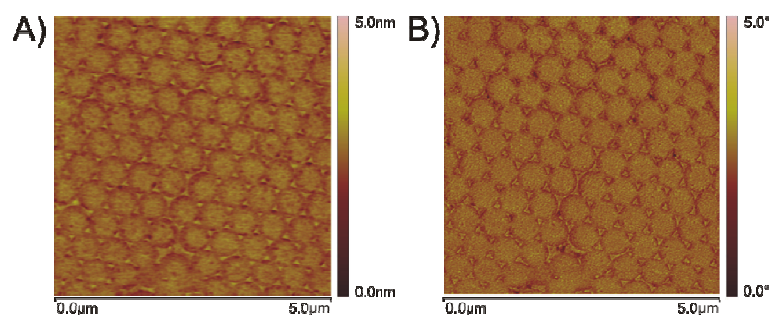


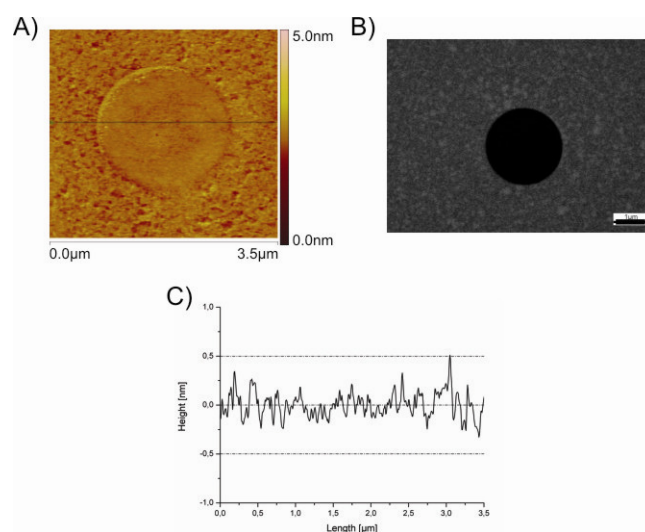
Figure S 2:  $^1\text{H}$ -NMR spectra of HC2TES(6)

## AFM pictures of structured substrates

The substrates used in this study for the template patterning of solid supported membranes were prepared accordingly to a previously described procedure.<sup>2</sup> The low roughness of these patterned substrates makes them ideal for solid supported membranes. AFM images of such structured substrates are presented in Figure S 3.



**Figure S 3: AFM pictures of substrates obtained by nanosphere lithography (550nm colloids) with a RMS roughness of 0.215 nm; A) height image, B) phase image.**

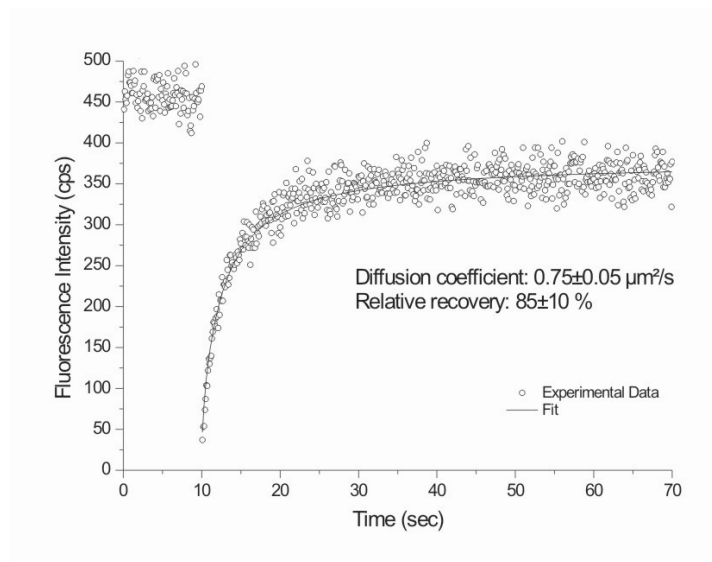


**Figure S 4: A) AFM, B) SEM and C) linescan of a substrate used for the construction of the membrane archipelagos; a SiO<sub>2</sub> disc embedded in a gold film is depicted.**

<sup>2</sup> N. Vogel, M. Jung, M. Retsch, W. Knoll, U. Jonas and I. Köper, *Small*, **2009**, 5, 821-825.

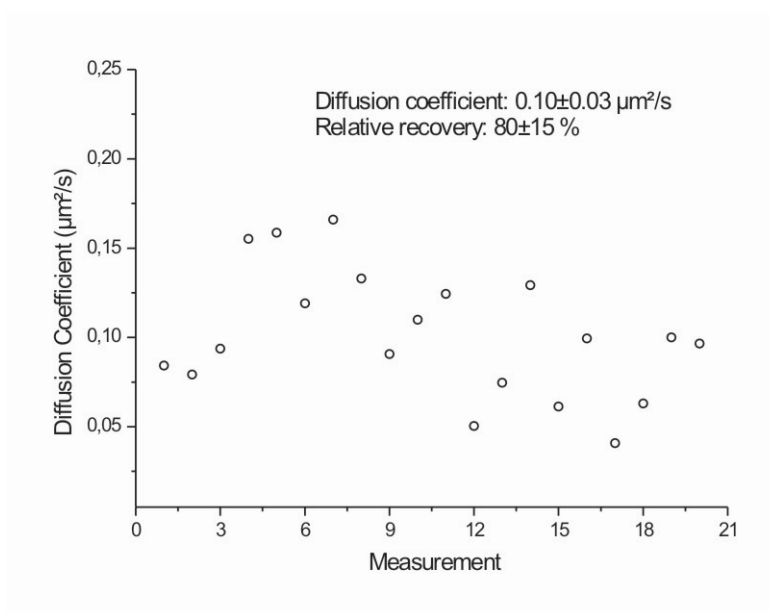
## FRAP of solid supported membrane

Figure S 5 presents a FRAP measurement on pure DPhyPC solid supported membrane on a clean silicon wafer, without obstacles.



**Figure S 5: FRAP measurement of DPhyPC solid supported membrane on a silicon wafer.**

Figure S 6 depicts the variance in the measurement series using a substrate produced with a colloidal monolayer of 550 nm.



**Figure S 6: Variance in the diffusion coefficients measurements on one membrane (template 550 nm colloids)**