Supporting information for

Langmuir-Blodgett Monolayer Stabilization Using Supramolecular Clips

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EXPERIMENTAL

General

All reactions were carried out under anhydrous conditions. All solvents were dried according to standard procedures and stored over molecular sieves. ^{1}H NMR spectra were recorded with a Bruker spectrometer 300MHz. Mass spectra were recorded in ESI mode on a thermoquest LCQ Deca instrument. TLCs were performed on pre-coated silica 0.2 mm. 25,26,27,28-tetrakis(tetradodecoxy)-5,11,17,23-tetramino-calix[4]arene (**1**) was produced as previously described.[1] N,N'-bis-tert-butoxycarbonylthiourea, was prepared according to the procedure reported in the literature.[2]

Synthesis of 5,11,17,23-Tetrakis[(bis-N-Boc)guanidine]-25,26,27,28-tetradodecyloxycalix[4]arene (2)

To a solution of **1** (5.13 g, 4.43 mmol) in dry CH_2Cl_2 (150 mL), N,N'-bis-tert-butoxycarbonylthiourea (5.14 g, 18.61 mmol), and Et_2N (6.73 g, 18.61 mmol) were added and the mixture was cooled in an ice bath. 2-chloro-1-methylpyridinium iodide (7.92 g, 31.01 mmol) was added and the mixture stirred 30 min at 0°C. The ice bath was removed and the reaction mixture was stirred overnight at 20 °C. The solvent was evaporated under reduce pressure and the residue was purified by flash column chromatography on silica gel (eluent: heptane/ethyl acetate 9:1 and 6:1) to obtain a pale yellow powder, **2** (4.14 mg, 44 %).

^{1}H NMR ($CDCl_3$-d ,300MHz): δ = 11.60 (s, 4 H, BocN*H*), 9.82 (s, 4 H, ArN*H*), 6.91 (s, 8 H, Ar*H*), 4.40 (d, *J*=12.9 Hz, 4 H, ArCH_2Ar), 3.84 (t, *J*=7.5 Hz, 8 H, OCH_2(CH_2)$_{10}$$CH_3$), 3.14 (d, *J*=13.1 Hz, 4 H, ArCH_2Ar), 1.91 (br. s., 8 H, OCH$_2$CH_2(CH_2)$_9$$CH_3$), 1.42 - 1.54 (m, 72 H, Bu^t), 1.28 (br. s., 72 H, O(CH_2)$_2$(CH_2)$_9$$CH_3$), 0.88 ppm (t, *J*=7.3 Hz, 12 H, O(CH_2)$_{11}$CH_3)

^{13}C NMR ($CDCl_3$-d ,75MHz): δ = 163.6, 154.0, 153.5, 153.0, 134.7, 130.7, 123.0, 86.7, 82.9, 79.0, 75.4, 31.9, 31.4, 30.1, 30.0, 29.8, 29.8, 29.7, 29.4, 28.2, 28.1, 26.3, 22.7, 14.1 ppm

MS (ESI) calculated m/z for $[M\text{-}8boc+H_2O+H]^+$=1344.07; found $[M\text{-}8boc+H_2O+H]^+$=1344.7; calculated $[M\text{-}8boc+2H]^{2+}$=663.5; found $[M\text{-}8boc+2H]^{2+}$=662.9.

Synthesis of 5,11,17,23-Tetrakisguanidinium-25,26,27,28-tetradodecyloxycalix[4]arene (GC12)

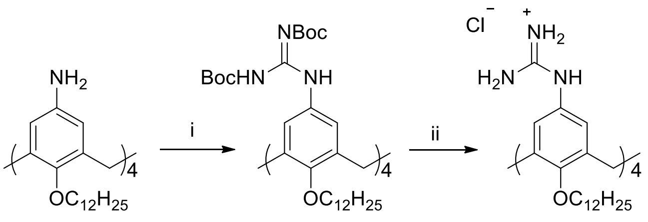
Concentrated HCl (37%) was added drop wise to a solution of **2** (2 g, 0.47 mmol) in 60 mL of 1,4 dioxane. The suspension was stirred 24h at room temperature and the solvent evaporated under vacuum. The obtained powder was triturated with ethyl acetate then filtrated, to give a beige powder in a yield of 69%.

^{1}H NMR (MeOD-d ,300MHz): δ = 6.68 (s, 8 H, Ar*H*), 4.51 (d, *J*=13.3 Hz, 4 H, ArCH_2Ar), 3.98 (t, *J*=7.2 Hz, 8 H, OCH_2(CH_2)$_{10}$$CH_3$), 3.28 (br. s., 2 H, ArCH_2Ar), 2.00 (br. s., 8 H, OCH$_2$CH_2(CH_2)$_9$$CH_3$), 1.18 - 1.70 (m, 72 H, O(CH_2)$_2$(CH_2)$_9$$CH_3$), 0.83 - 0.99 ppm (m, 12 H, O(CH_2)$_{11}$CH_3)

^{13}C NMR (MeOD-d ,75MHz): δ = 158.0, 157.3, 137.8, 130.0, 126.8, 77.1, 33.3, 31.9, 31.5, 31.3, 31.3, 31.1, 30.8, 28.0, 24.0, 14.6 ppm

TLC heptane/ ethyl acetate (4:1) Rf= 0.4.

MS (ESI) calculated m/z for $[M\text{-}4HCl+2H]^{2+}$= 663.53, found $[M\text{-}4HCl+2H]^{2+}$= 662.9.



1 **2** **GC12**

Figure S1: Synthetic route to **GC12**; reagents and conditions: (i) Boc-NH-C(S)-NH-Boc, Mukaiyama's reagent in CH_2Cl_2 , rt; (ii) HCl/1,4-dioxane, rt.

Langmuir monolayer experiments

Prior to experiments, the Langmuir trough (Nima 112D) and the barriers were cleaned with analytical grade chloroform and nanopure water (resistivity $\geq$18 MΩ.cm). The microbalance was calibrated before each series of runs using a weighing pan and a calibration weight. Clip solutions, at defined concentration in nanopure water, were prepared extemporaneously. The absence of surface-active molecules was controlled by closing the barriers in the absence of **GC12**; no relevant change in surface tension was observed. 10µL of **GC12** solution in chloroform (1 mg mL^{-1}) was spread on the liquid subphase using a gastight microsyringe. 15 min was allowed for solvent evaporation and monolayer equilibration; barriers were closed in continuous mode at a speed rate of 5 cm^2min^{-1}.

Langmuir-Blodgett transfer procedure

Langmuir-Blodgett transfers were performed using a vertical dipping system (speed rate 5 mm min^{-1}). Experiments were carried out in surface tension controlled mode (35 mN m^{-1}). Silicon wafers were used as solid substrates for LB deposition. After cutting the silicon wafers, they have been first pre-cleaned using soap, nanopure water, acetone and methanol respectively. Pre-cleaned silicon wafers were places 20 min in a UV/ozone chamber consecutively rinsed with methanol and dried under a nitrogen stream. The so-cleaned substrates were immersed for 30 min in 3.9 g L^{-1} anhydrous heptane solution of octadecyltrichlorosilane, rinsed and submitted to an ultrasonic treatement for 10 min in heptane and chloroform respectively. **GC12** LB monolayer was transferred on hydrophobic Si/SiO_2 wafer at controlled dipping speed rate (5 mm min^{-1}) and surface tension (35 mN m^{-1}). After 60 min of equilibration time in the subphase, the monolayer at the interface was removed by suction and the substrate was removed at a speed rate of 50 mm min^{-1}. Coated Si/SiO_2 wafers were rinsed after 2 hours with nanopure water (pH 8).

Spectroscopic ellipsometry

Ellipsometry measurements were carried out using an imaging and spectroscopic system (EP^3 Ellipsometer, Accurion) in a nulling PCSA (polarizer-compensator-sample-analyzer) set-up. In this system, the incident beam that is elliptically polarized with a linear polarizer (P) and a quarter-wave plate (C) is reflected from the sample (S) to the analyzer (A) and finally imaged with a CCD camera using 10× objective. The nulling conditions, related to the optical properties of each sample, were obtained by tuning the angles of P, C and A. Measured data were then converted to the Δ (relative phase shift of *p*- and *s*-polarized light upon reflection on the sample) and Ψ (relative amplitude ratio of the reflection coefficients of *p*- and *s*- polarization). Measurements were performed with a fixed angle of incidence (50°) at five different wavelengths (λ=629.1, 710.2, 791.2, 880.7, 1000.8 nm). Transferring measured Δ and Ψ as a function of wavelength lambda to the EP^4 model, thickness of transferred layers could be calculated. A model with four layers

(Si/SiO_2/OTS/LB/air) was created. Using data base of EP^4 software, dispersion functions of SiO_2, Si and air as ambient were defined. A Cauchy model with predefined refractive index and extinction coefficient (n= 1.5, k=0) has been designated for the LB and OTS layers. Thickness of 30 Å and 28 Å was measured for SiO_2 and OTS layer, respectively. A system control was done prior to each set of experiments using standard Si/SiO_2 samples.

Contact angle measurement

The contact angle was measured using a commercial Krüss Easy drop optical system (Krüss, GmbH, Germany). 5µL of nanopure water drops were used for measuring static water contact angle on coated samples. To ensure reproducibility, the measurements were repeated at 5 different positions on each sample.

Atomic force microscopy

Coated samples, after rinsing with nanopure water (pH 8), were imaged by atomic force microscopy in tapping mode using a Multimode 5 instrument (Bruker AXS) equipped with a Nanoscope IIIa controller; MicroMash NSC15 silicon tips were used.

X-ray photoelectron spectroscopy

XPS was measured in normal emission using monochromatic Al Kα (hν = 1486.7 eV) excitation (Specs FOCUS 500) in normal emission using a Specs PHOIBOS 150 electron analyzer. The full with half maximum of the instrumentation was 0.8 eV. To reduce sample charging, a flood-gun was used to provide free electrons. The Si2p core level of the substrate was used as reference for the binding energies and was assigned to 99.3 eV for Si^0 respectively. The intensities and thus the stoichiometric ratios were calibrated using an in-situ prepared reference containing C, N and F. The measurements were performed in ultra-high vacuum (~ 10^{-10} mbar).

RESULTS

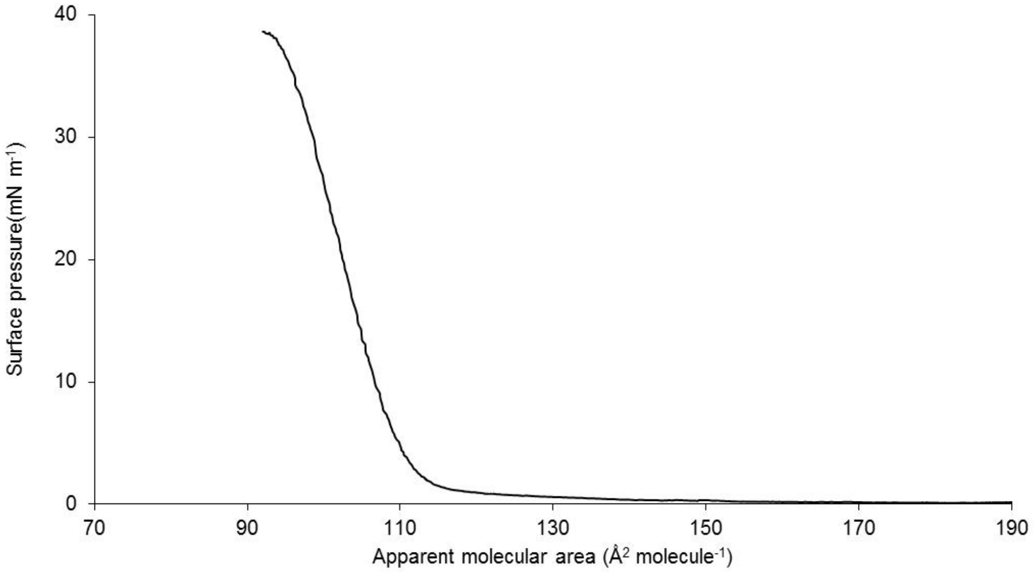


Figure S2: Π/A isotherm of **GC12** measured on water

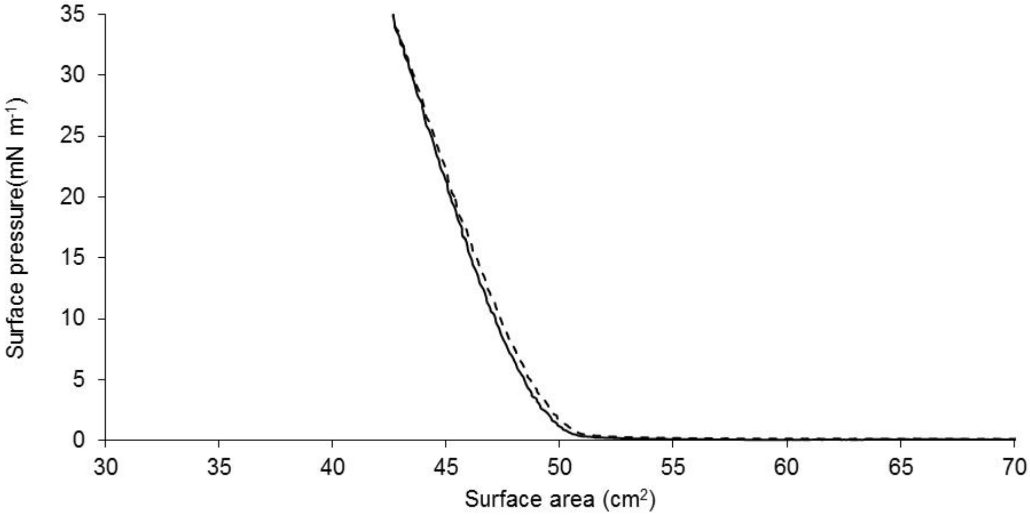


Figure S3: Surface pressure vs surface area of **GC12** Langmuir monolayer measured on 0.166 g L^{-1} *ortho*-phthalic acid, compressed at a speed rate of 5 cm^2 min^{-1} with a target pressure (35 mN m^{-1})

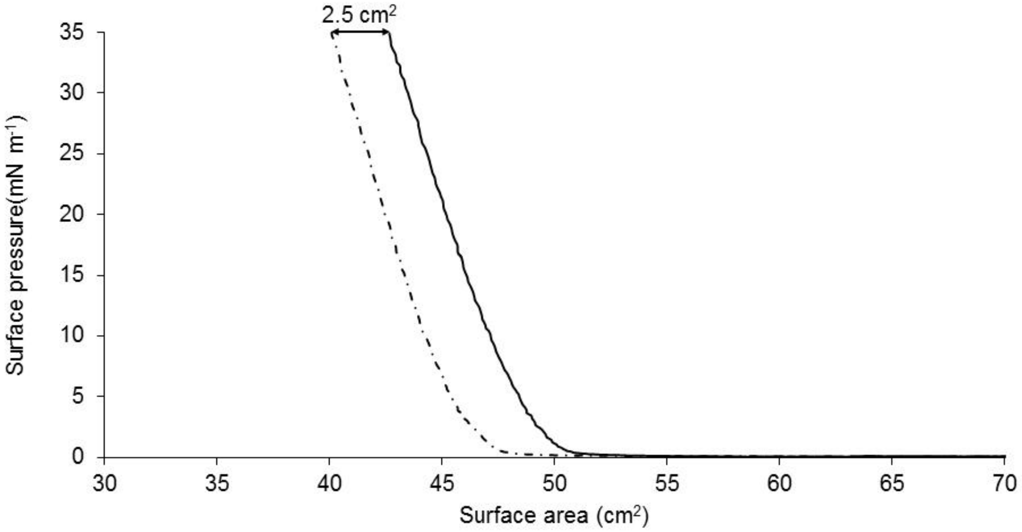


Figure S4: Surface pressure vs surface area measurement (—) before and (–·–) after transfer of **GC12** Langmuir monolayer on solid substrate using 0.166 g L^{-1} *ortho*-phthalic acid solution.

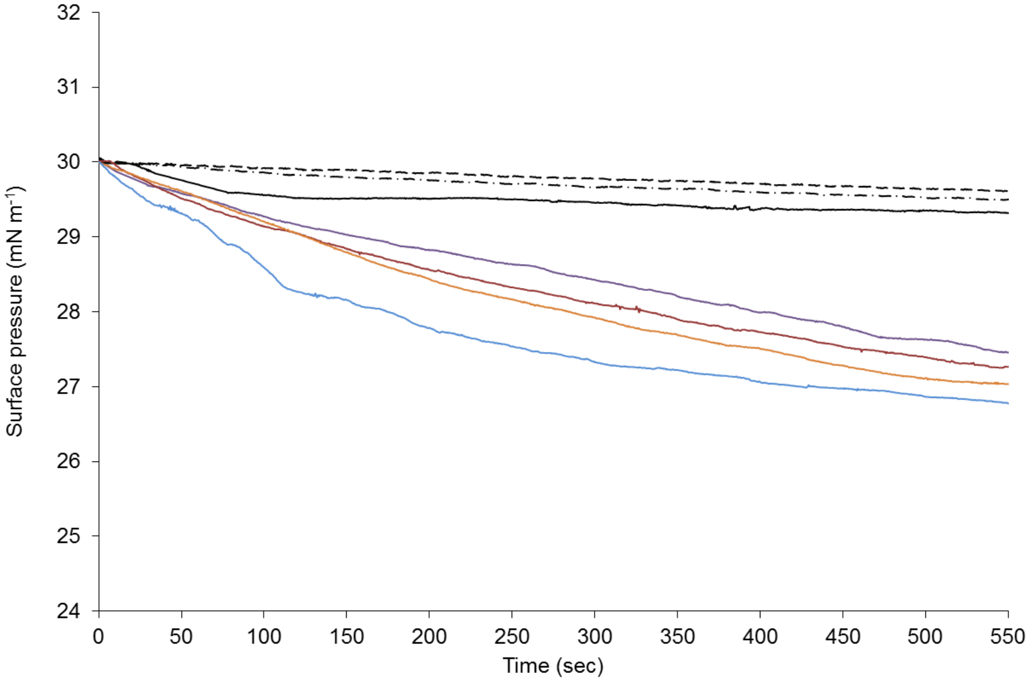


Figure S5: Surface pressure in function of time for monolayers of **GC12** measured on pure water (—) and subphases of *para*-phthalic (0.1mM, —), benzoic (1mM, —), fumaric (1mM, —), *ortho*-phthalic (1mM, —), succinic (1mM, –·–) and maleic (1mM, --) acids subphases. Compressions were carried out at a speed rate of 5 cm^{2}min^{-1} and stopped when the surface pressure reached a value of 30 mN m^{-1}.

Table S1 Average decay measured for the isotherms of **GC12** prepared on water and subphases of **1**, **2**, **3**, **5**, **6** and **7**.

Subphase additive	Additive concentration (mM)	Average measured decay mN/(m.min)
-	0	0.33
1	1	0.077
2	0.1	0.31
2*	1	*n.d.*
3	1	0.29
5	1	0.26
6	1	0.041
7	1	0.052

*Average decay using **2** at 1mM could not be measured (*n.d.*) because of the poor solubility of this compound in water.

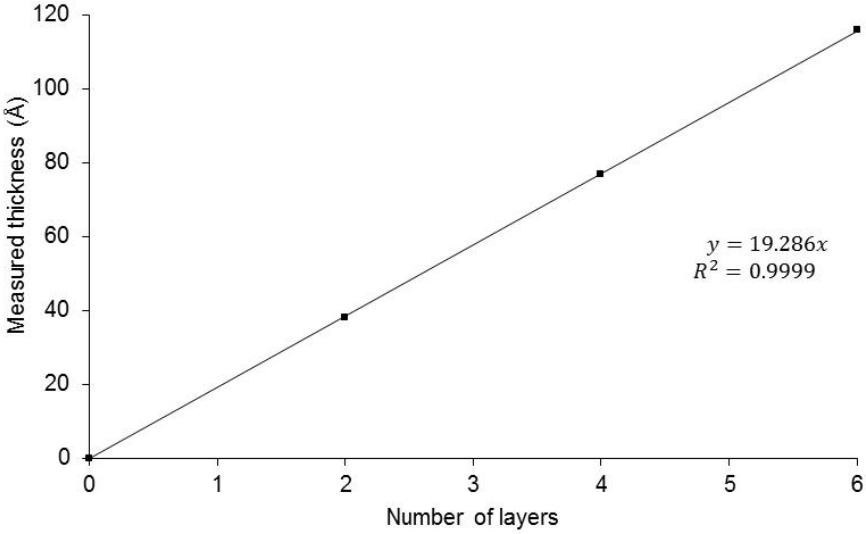


Figure S6: Layer thickness measured for LB bilayers transferred using water as subphase.

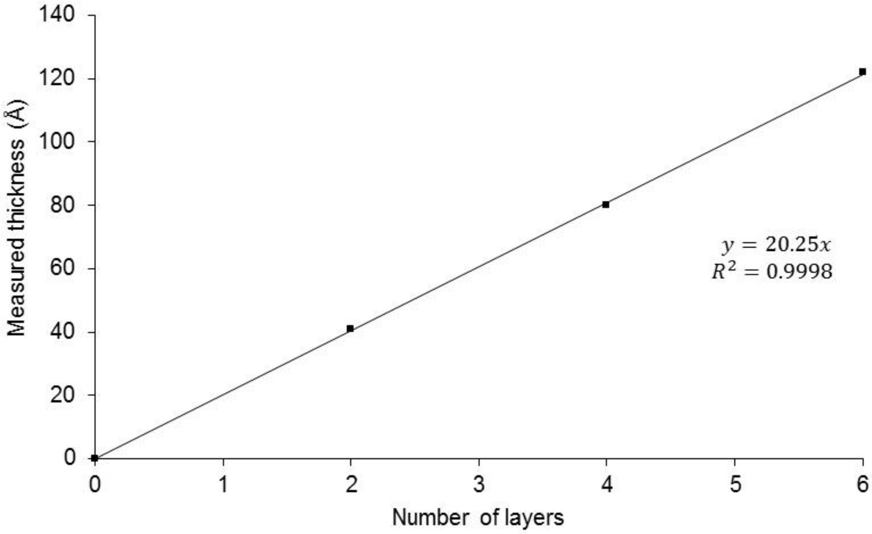


Figure S7: Layer thickness measured for LB bilayers transferred using 0.166 g L^{-1} *ortho*-phthalic acid as subphase.

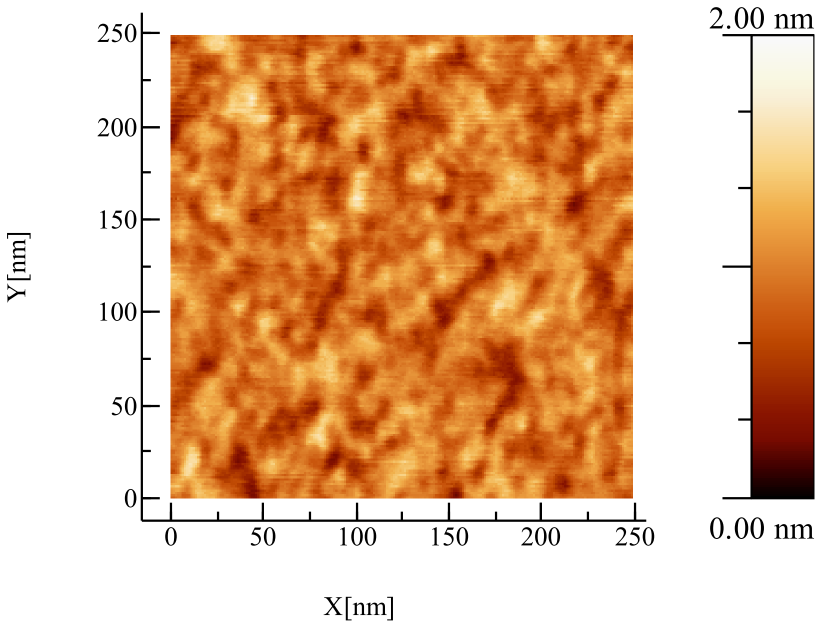


Figure S8: AFM tapping mode micrograph of OTS-modified Si/SiO_2 substrate (RMS roughness: 0.17 nm)

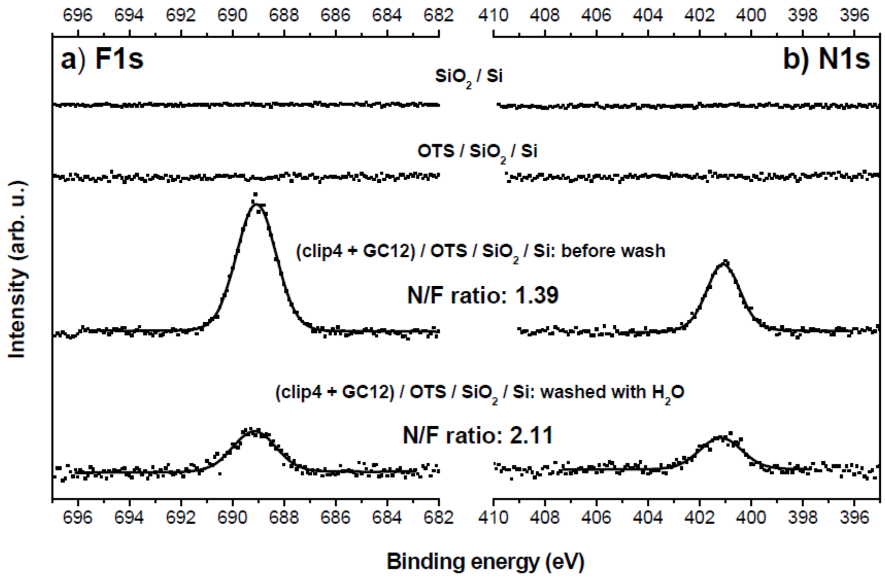


Figure S9: F1s (a) and N1s (b) XP spectra: The core level signals are used to track the composition and stoichiometry of the **GC12** LB films (N1s) and 4-trifluoromethyl-*ortho*-phthalic acid (F1s), respectively.

NB: In the bare SiO_2/Si substrate and in the octadecyltrichlorosilane (OTS) monolayer on SiO_2/Si, no N1s and F1s signal was observed. In the **GC12** + **4** LB film prior to washing, the observed N/F ratio of 1.39 indicated an excess of the **4** molecule. After wash with H_2O, the N/F ratio is 2.11. This is in good agreement with the ideal value of 2 for a 2:1 complex of **4** (3 F) and **GC12** (12 N).

(1) Shahgaldian, P.; Sciotti, M. A.; Pieles, U. *Langmuir* **2008**, *24*, 8522.
(2) Bianco, A.; Brufani, M.; Dri, D. A.; Melchioni, C.; Filocamo, L. *Lett. Org. Chem.* **2005**, *2*, 83.