Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Electrochemically driven host-guest interactions on patterned donor/acceptor self-assembled monolayers

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Figure S10. Confocal microscope images of the functionalised substrates after interaction with F-β-CD.

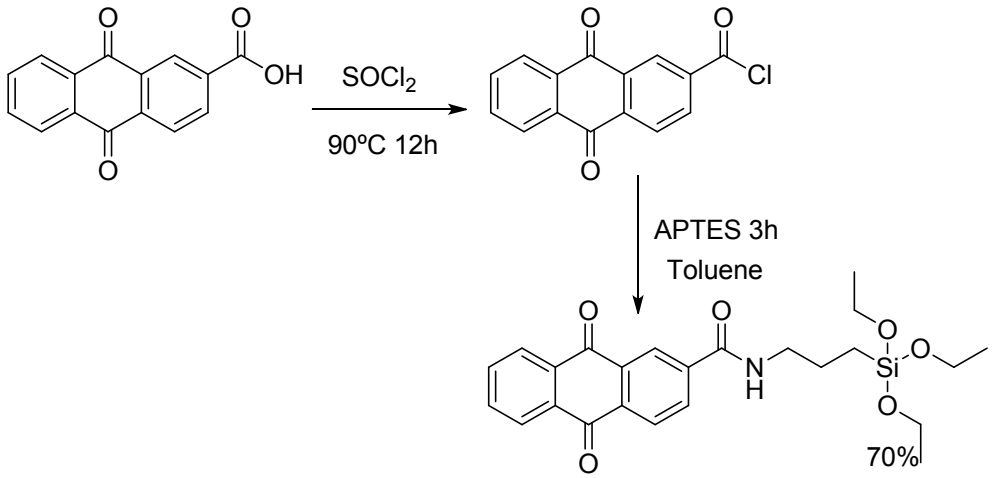
1.Experimental methodologies

1.1. Molecules and solvents

F-β-CD and β-CD were purchased, respectively, from *Cyclolab* and Chemika. All the molecules were used as received without further purification.

All the solvents used for SAM preparation were HPLC pure grade and were supplied by Teknokroma.

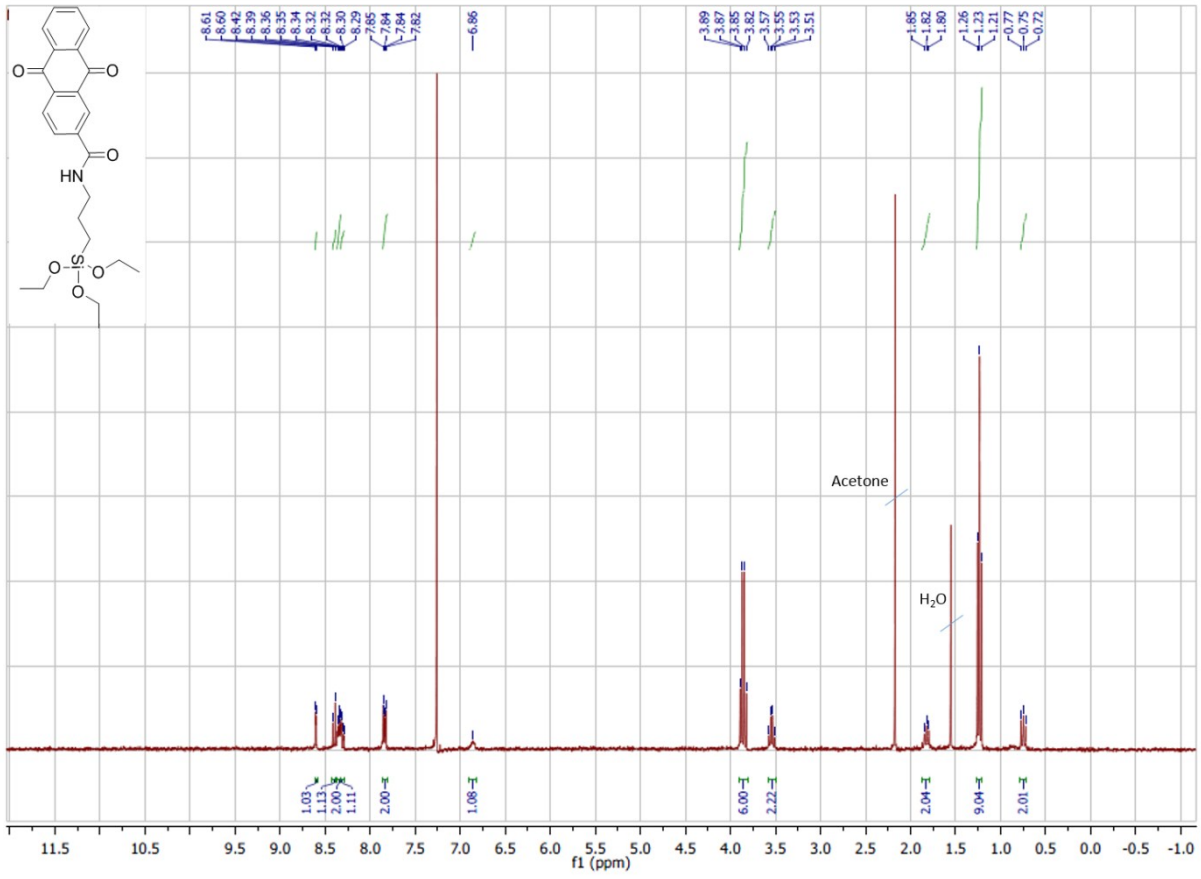
1.2 Synthesis of 9,10-dioxo(triethoxysilyl)propyl)-9,10-dihydroanthracene-2-carboxamide (AQSi)[i]

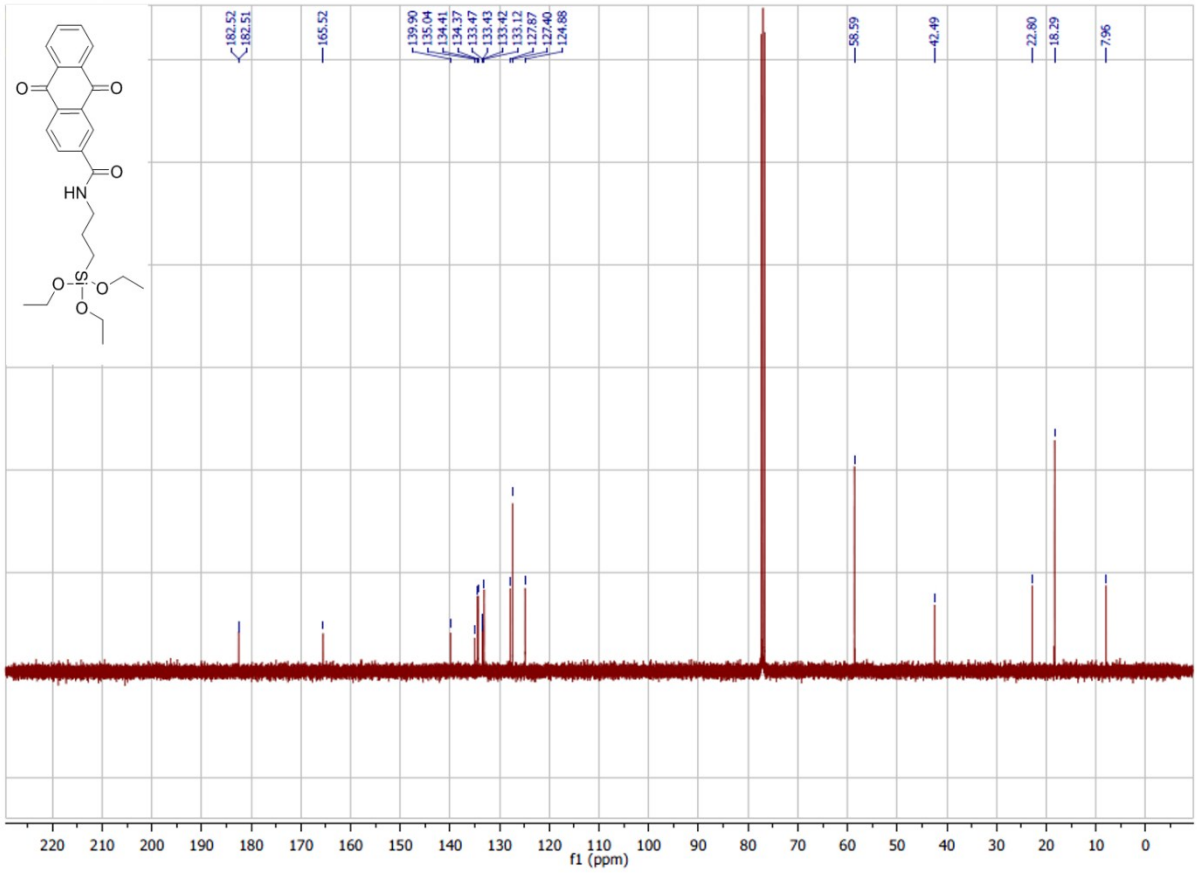


300 mg of anthraquinone-2-carboxylic acid (1.2 mmol) is dissolved in 5 mL of $SOCl_2$ under inert atmosphere and the mixture is stirred overnight at reflux temperature. The excess of $SOCl_2$ is then removed flowing nitrogen. The solid thus obtained is subsequently dissolved in 20 mL of dry toluene. APTES and NEt_3 is then added.The mixture is stirred for 3h. After that the solvent is removed under vacuum and the solid obtained is dissolved in chloroform. Successive precipitations and filtrations in an ether/hexane mixture are carried out to remove tri-ethyl ammonium chloride. AQSi is obtained in a 70% of yield.

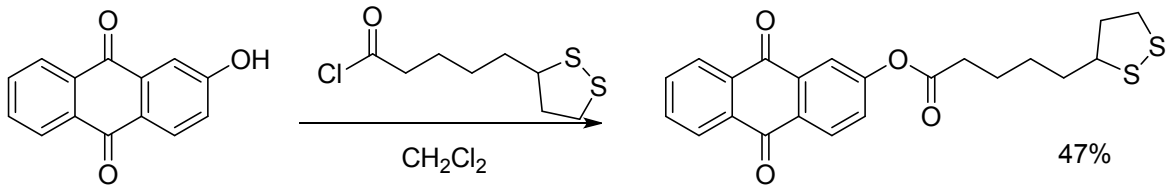
^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 8.60 (d, *J* = 1.7 Hz, 1H), 8.40 (d, *J* = 8.1 Hz, 1H), 8.37 – 8.33 (m, 2H), 8.31 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.84 (m, 2H), 6.86 (bs, 1H), 3.86 (q, *J* = 7.0 Hz, 6H), 3.54 (q, *J* = 6.5 Hz, 2H), 1.86 – 1.78 (m, 2H), 1.23 (t, *J* = 7.0 Hz, 9H), 0.77 – 0.72 (m, 2H).

^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 182.52, 182.51 (C=O AQ), 165.5 (C=O amide), 149.9-124.9(C-Ar), 58.6, 42.5, 22.8, 18.3, 7.9



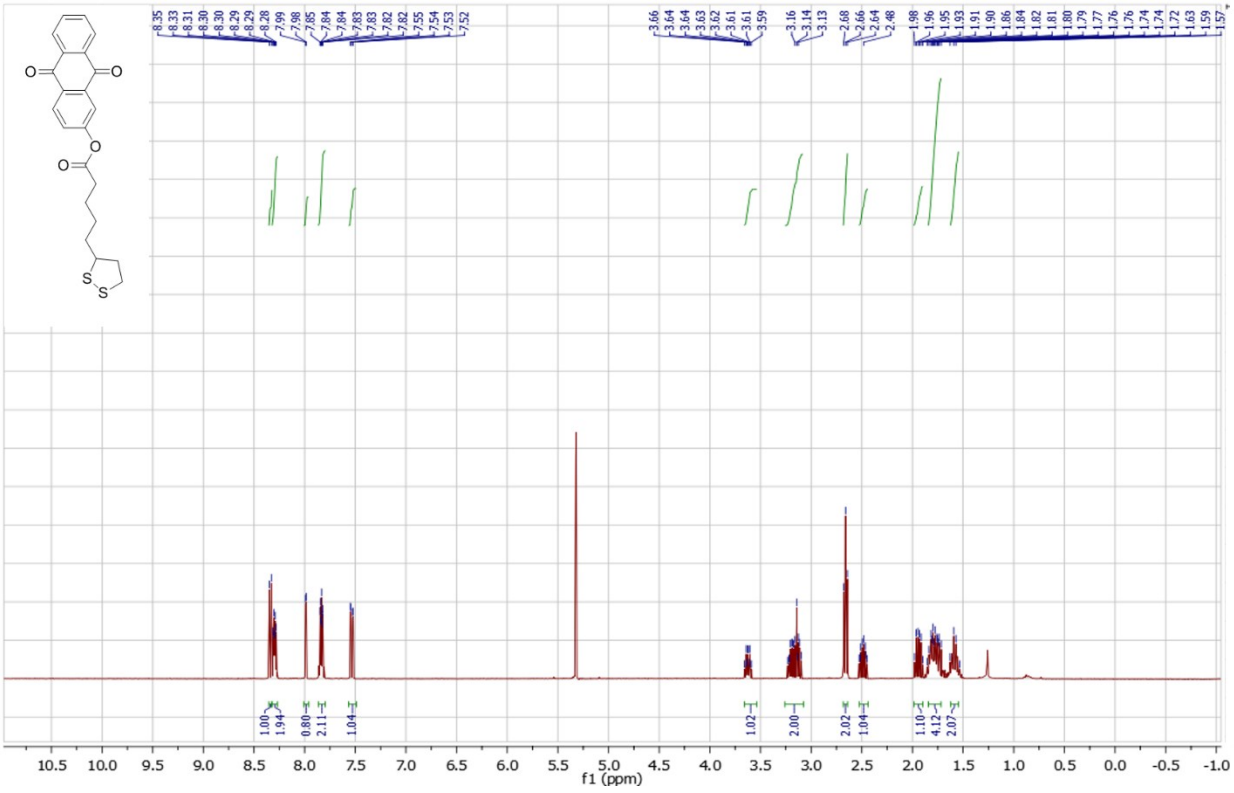


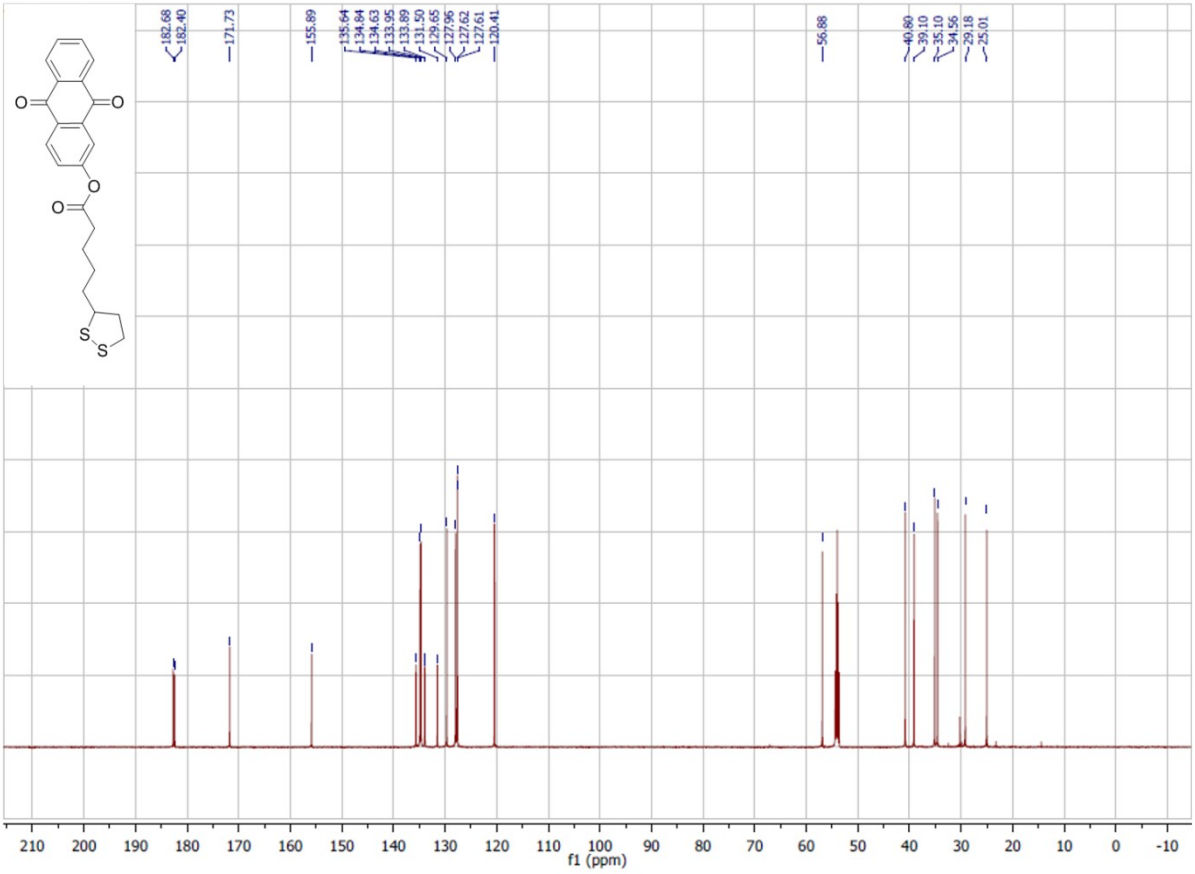
1.3. Synthesis of 9,10-dioxo-9,10-dihydroanthracen-2-yl 5-(1,2-dithiolan-3-yl)pentanoate (AQS_2)[ii]



2-hydroxyanthracene-9,10-dione (0.205g 0.915 mmol) is dissolved in dry dichloromethane (60 mL) and 0.2 mL (1.49 mmol) of NEt_3 are then added dropwise. The mixture is stirred at 0°C for 15 min. under Ar atmosphere. After addition of α-lipoic acid chloride (0.272 g, 1.20 mmol), dissolved in dry CH_2Cl_2 (4 mL), the mixture is stirred overnight at room temperature and the residue purified by a chromatography column (silica-gel, CH_2Cl_2) giving the compound AQS_2 (0.158 g, 47%) as a yellow powder.

^{1}H NMR (400 MHz, CD_2Cl_2) δ (ppm): 8.34 (d, *J* = 8.34 Hz, 1H), -8.32-8-27 (m, 2H), 7.99 (d, *J* = 2.4 Hz 1H), 7.86-7.80 (m, 2H), 7.53 (dd, , *J* = 8.5, 2.4 Hz 1H), 3.66-3.59 (m, 1H), 3.26-3.08 (m, 2H), 2.66 (t, *J* = 7.4 Hz, 2H), 2.53- 2.44 (m, 1H), 1.98-1.90 (m, 1 H), 1.84-1.72 (m, 4H), 1.63-1.53 (m, 2H); ^{13}C NMR (600 MHz, CD_2Cl_2) δ (ppm): 182.7 (C=O AQ), 182.4, (C=O AQ), 171.7 (C=O ester), 155.9, 135.6-120.4 (C-Ar), 56.9, 40.1, 39.1, 35.1, 34.6, 29.2, 25.0





1.4. Patterned substrate fabrication

Glass substrates coated with ITO were used (Code: CG-50IN-0105, Delta Technologies, dimensions: 25 x 25 x 0.55 mm). To pattern the ITO, the gold was evaporated through a metallic mask. The metallic mask was fixed on the ITO substrate using a magnetic support, subsequently chromium (15 nm) and gold (70 nm) was deposited (BOC Edwards Auto 360). Finally, the substrate was rinsed with ethanol, isopropanol and drying with nitrogen.

2.Surface modification

2.1. Materials

A commercial substrate of 50 nm of polycristallyne gold evaporated on glass adhesive layer provided from Phasis and a commercial substrate of 70 nm of ITO on glass bought from Delta Technologies, were used as platform for the preparation of the mono-component $FcSH_{dil}$-SAM and AQSi-SAM, respectively. Gold substrates for SPR were used as platforms for the fabrication of AQS_2-SAM.

2.2. Surface cleaning

All substrates were degreased in a solvent series (dichloromethane, acetone and ethanol HPLC pure grade) with ultra-sonication for fifteen minutes each. Then the substrates were rinsed with ethanol and dried under nitrogen stream. The ITO substrate activation was realised by keeping the substrate in an ozone cleaner chamber during 20 min. During the SAM preparation, all the solutions were kept under argon atmosphere.

2.3. Preparation of $FcSH_{dil}$-SAMs

Cleaned gold substrates were immersed overnight in a solution 2 mM of FcSH:C_{10}SH 1:9 in ethanol at room temperature. After this time, the substrates were rinsed thoroughly with ethanol and dried under nitrogen stream.

2.4. Preparation of AQSi-SAM

The freshly activated ITO substrates were immediately immersed for 4 hours in a solution 0.5 mM of AQSi in toluene at room temperature. Then they were rinsed thoroughly with toluene and dried under nitrogen stream.

2.5. Preparation of AQS_2-SAM

The cleaned gold substrate was immersed in 0.5 mM solution of AQS_2 in THF during 40 h. Then the substrates were rinsed thoroughly with THF and dried under nitrogen stream.

2.6. Preparation of AQSi//$FcSH_{dil}$ SAMs on patterned ITO//Au substrates

The patterned substrates were rinsed thoroughly with ethanol and isopropanol and dried under nitrogen stream. Then the substrates were cleaned and activated in the ozone chamber. Immediately afterwards, the substrates were immersed in 0.5 mM of AQSi solution in toluene for 4 hours under inert atmosphere. The ITO functionalized patterned substrates were then rinsed thoroughly with toluene and ethanol, dried under nitrogen stream and immersed in a 2 mM solution of of FcSH:C_{10}SH 1:9 in ethanol overnight. The final functionalized substrates were rinsed thoroughly with ethanol and dried under nitrogen stream.

3. Procedures and apparatus

3.1. XPS Measurements.

X-ray photoelectron spectroscopy measurements were done with a Phoibos 150 analyzer (SPECS GmbH, Berlin, Germany) in conditions of ultra-high vacuum (base pressure $5x10^{-10}$ mbar) with a monochromatic aluminium Kalpha X-ray source (1486.74 eV). The energy resolution measured by the FWHM of the Ag 3d5/2 peak for a sputtered silver foil was 0.6 eV. The spot size was 3.5 mm by 0.5 mm.

3.2. SPR

Gold substrates for SPR spectroscopy were used as platforms for the fabrication of AQS_2-SAM. SPR was carried out on a spectrometer SR7000DC (Reichert, Buffalo, USA). SPR substrates (1.44 cm2 x 0.3 mm) consist of glass with a 50 nm thick gold layer and have a refractive index of 1.5168 (Xantec SC AU, Xantec bioanalytics, Kevelaer-Kervenheim, Germany).

3.3 CV measurement

The measurements of cyclic voltammetry (CV) were carried out using a potentiostat/galvanostat 263a (EG&G Princeton Applied Research). A conventional three-electrode setup was used. The modified substrates were used as the working electrode (WE), while a platinum and a silver wires (0.5 mm of diameter each one) were used as counter (CE) and quasi-reference electrodes (RE), respectively.

3.4 Contact Angle measurement

The static contact angle measurements were done using Drop Shape Analyzer DSA 100 from KRÜSS. 5 µL droplets were deposited on the modified surfaces.

3.5 AFM images

Atomic force microscope (AFM) images were obtained working with a 5100 SPM system from Agilent technologies in tapping mode and the images were analyzed using Gwyddion 2.47 software.

3.6 Fluorescence measurements

Fluorescence measurements were performed using Leica SP5 confocal microscope with HCX PL APO CS 10.0 x 0.40 DRY UV objective and emission bandwidth of 500-571 nm. The images were analyzed using the software Leica LAS AF Lite.

4. Supporting information figures

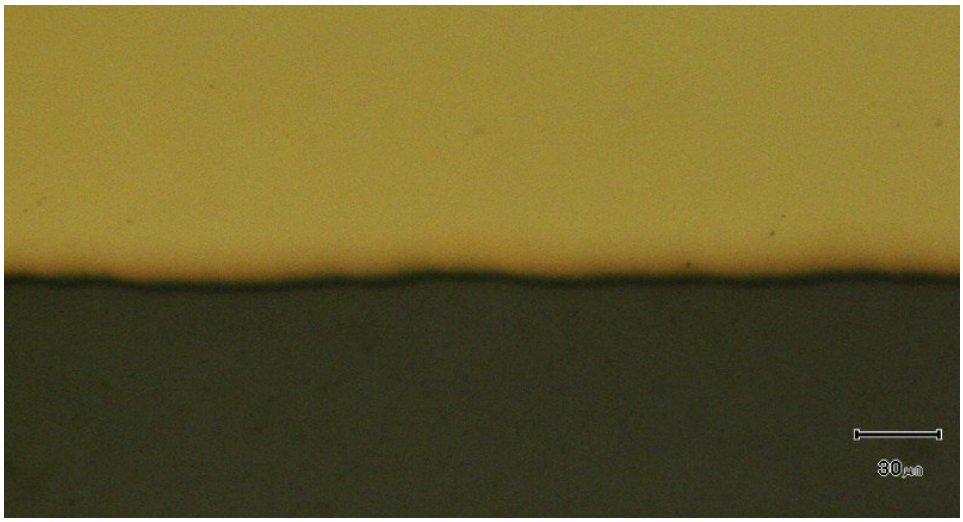


Figure S1: Optical microscope image of patterned substrate ITO//gold obtained through gold evaporation using the homemade mask.

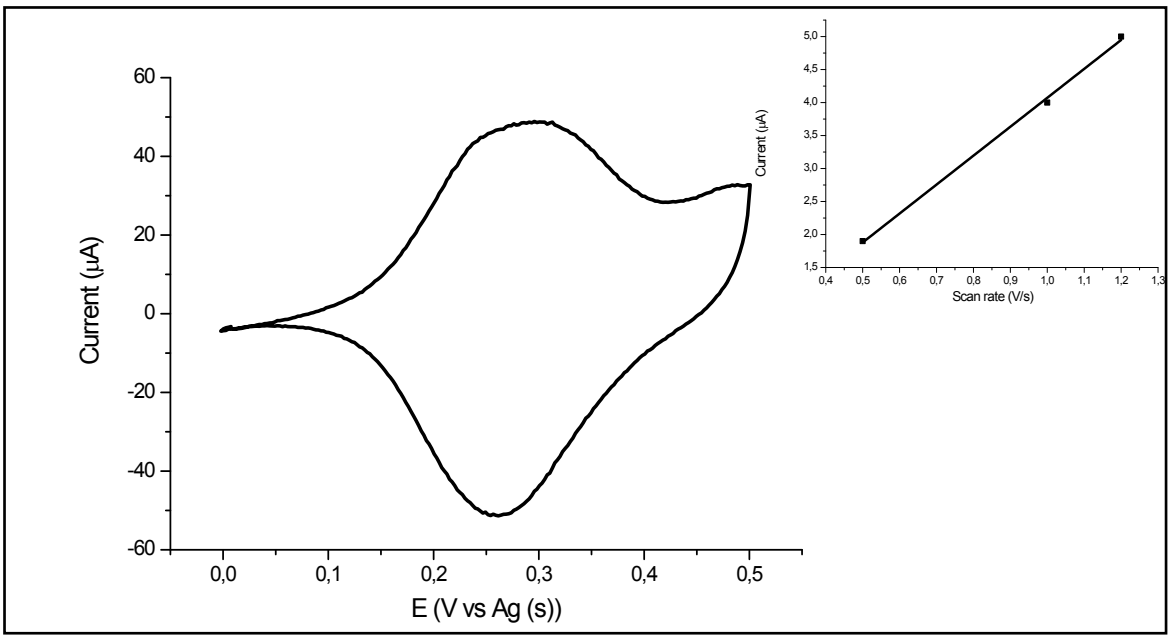


Figure S2: Cyclic voltammetry of $FcSH_{dil}$-SAM on Au. $FcSH_{dil}$ was used as the working electrode while a platinum and a silver wires were used as counter and quasi-reference electrodes, respectively. Phosphate buffer solution at pH 6.9 was employed as electrolyte. Inset: Current intensiy *versus* scan rate.

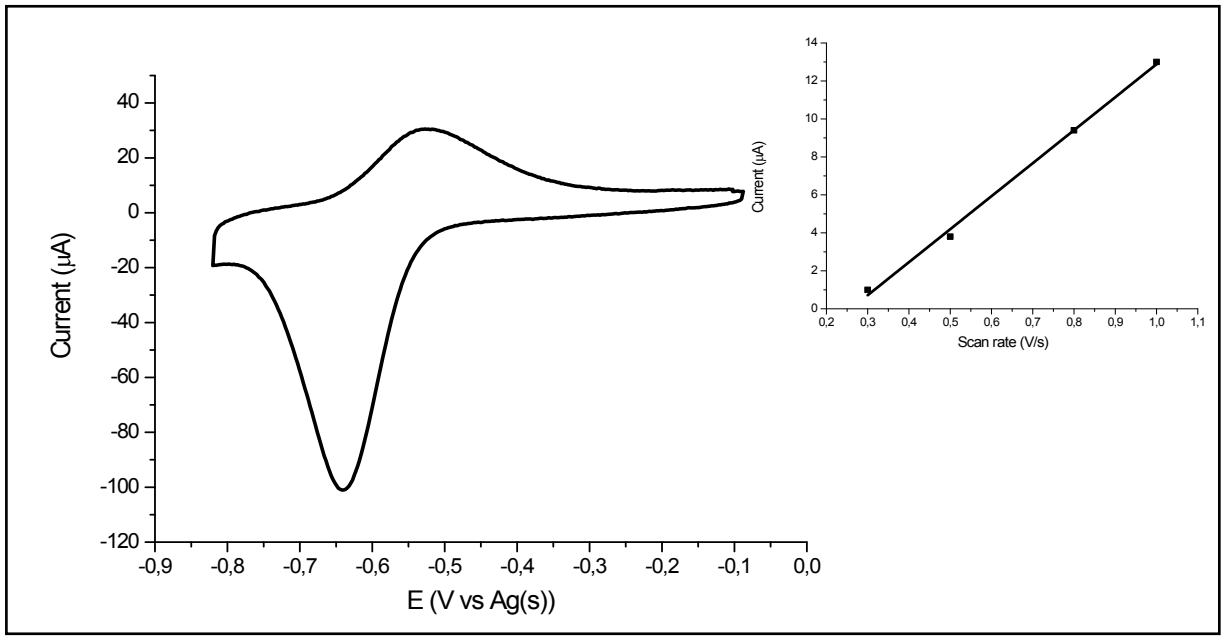


Figure S3: Cyclic voltammetry of AQSi-SAM on ITO. AQSi-SAM was used as the working electrode, a platinum wire as counter electrode and a silver wire as quasi-reference, respectively. Phosphate buffer solution at pH 6.9 was employed as electrolyte. Inset: Current intensiy *versus* scan rate.

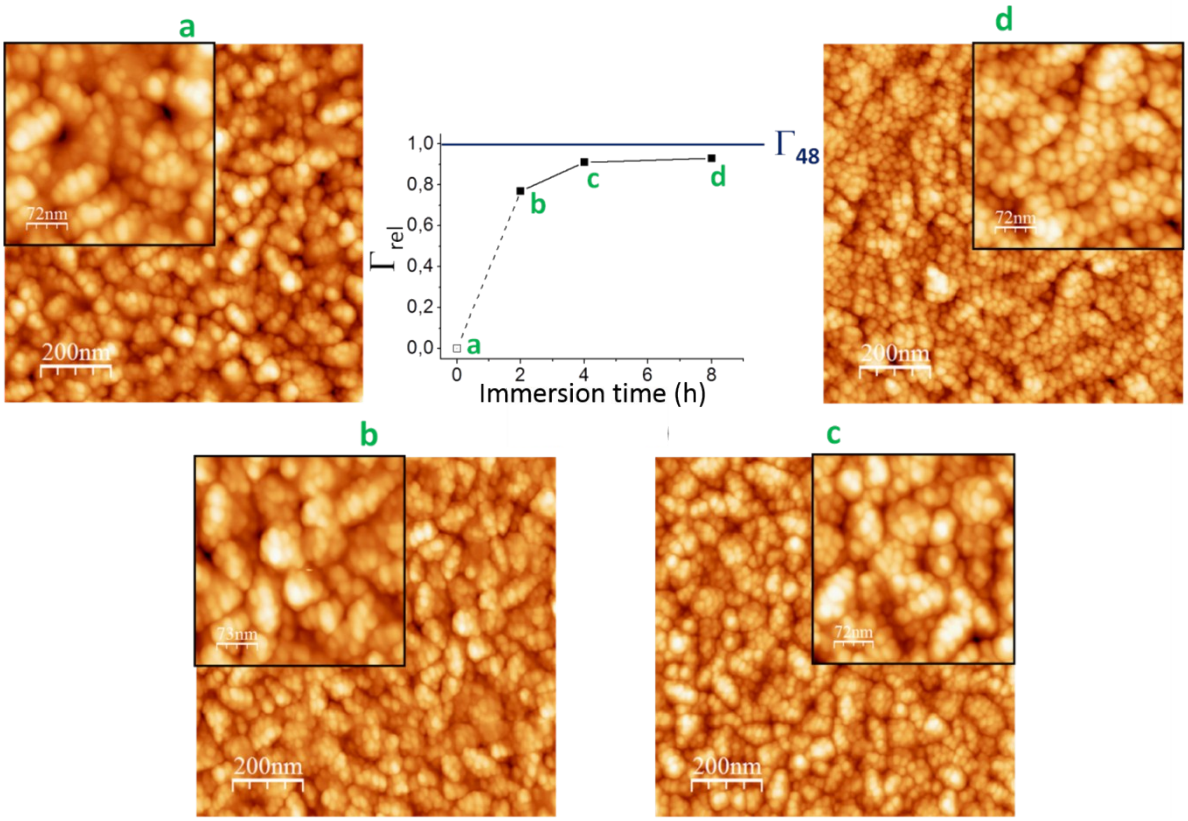


Figure S4: Variation of the relative surface coating (Γ_{rel}) of AQSi-SAM with increasing the immersion time of the substrate in the AQSi solution during b) 2, c) 4, and d) 8 hours. AFM topography images (1x1 μm^2) of AQSi-SAM on ITO (b-d) and of the unfunctionalized ITO substrate (a).

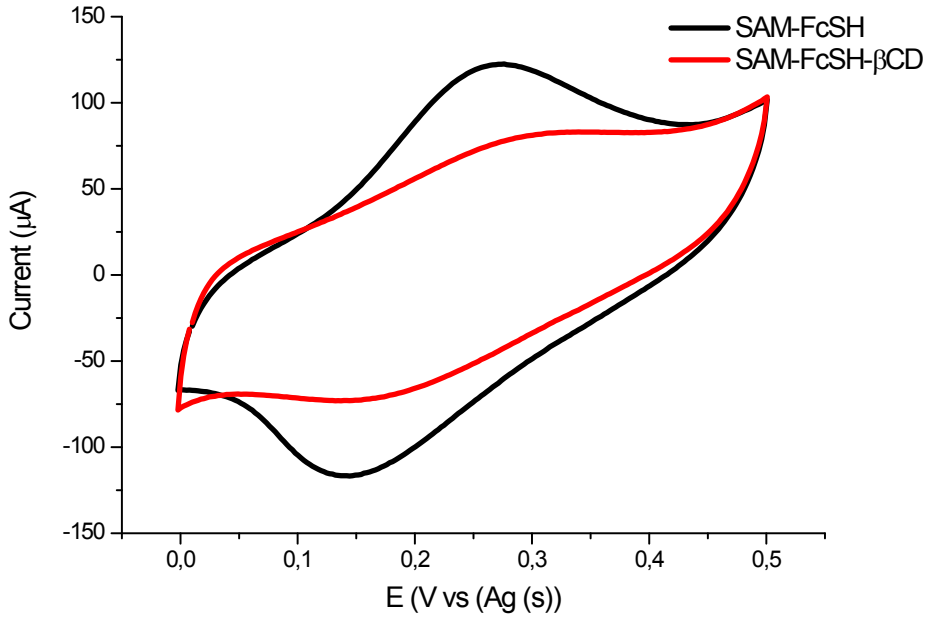


Figure S5: Study of the interaction between β-CD and the $FcSH_{dil}$-SAM followed by cyclicvoltammetry. The CV curve of $FcSH_{dil}$-SAM on Au was registered before (black line) and after (red line) immersion in a 9 mM solution of β-CDs in ultrapure water for 3h. After the immersion the substrate was washed under 50 mL of ultrapure water and dried under nitrogen stream. $FcSH_{dil}$-SAM on Au was used as working electrode. The quasi-reference and the counter electrodes used were silver and platinum wires, respectively. A phosphate buffer solution (pH 6.9) was used as electrolyte.

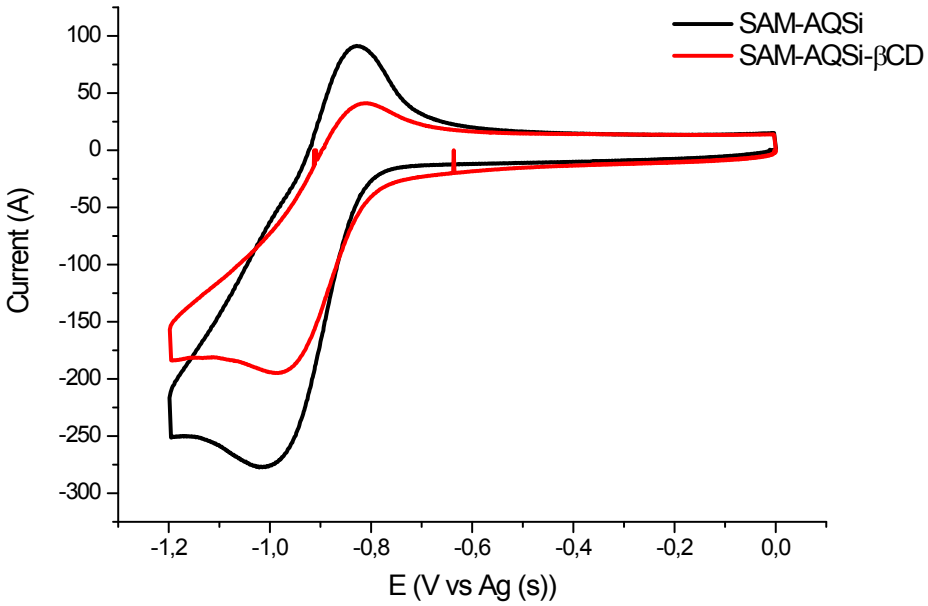
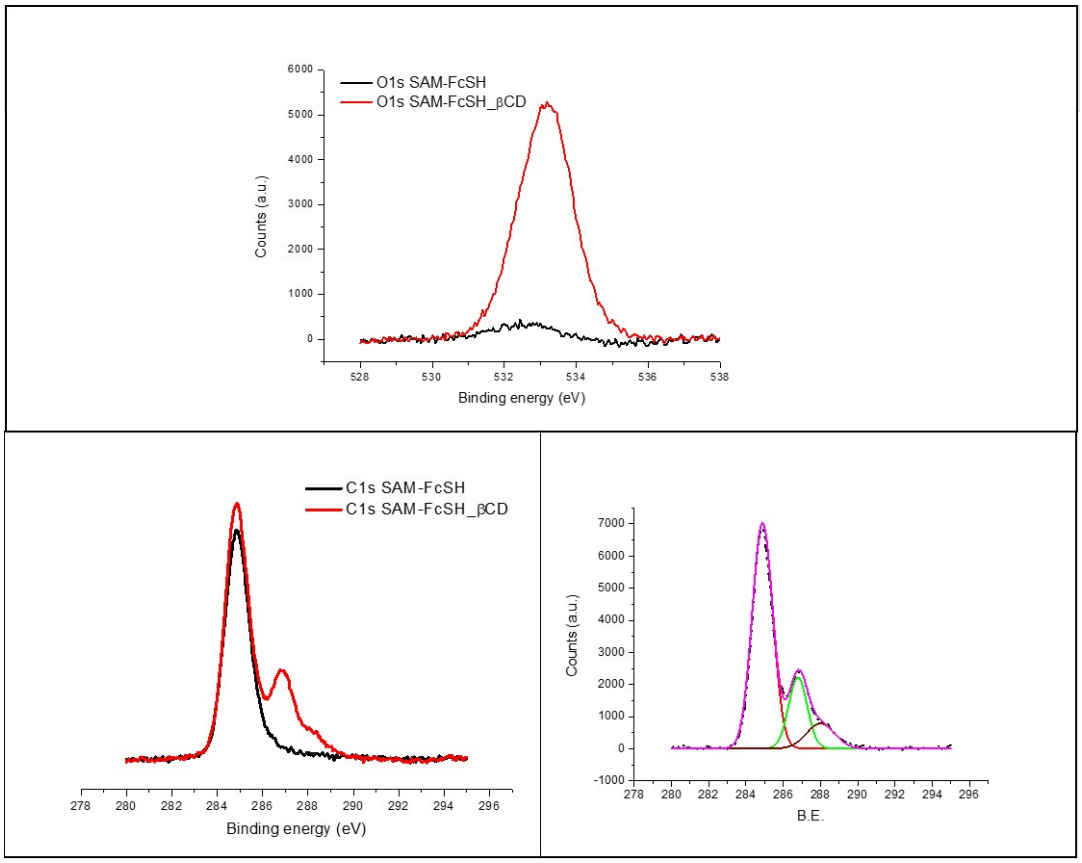
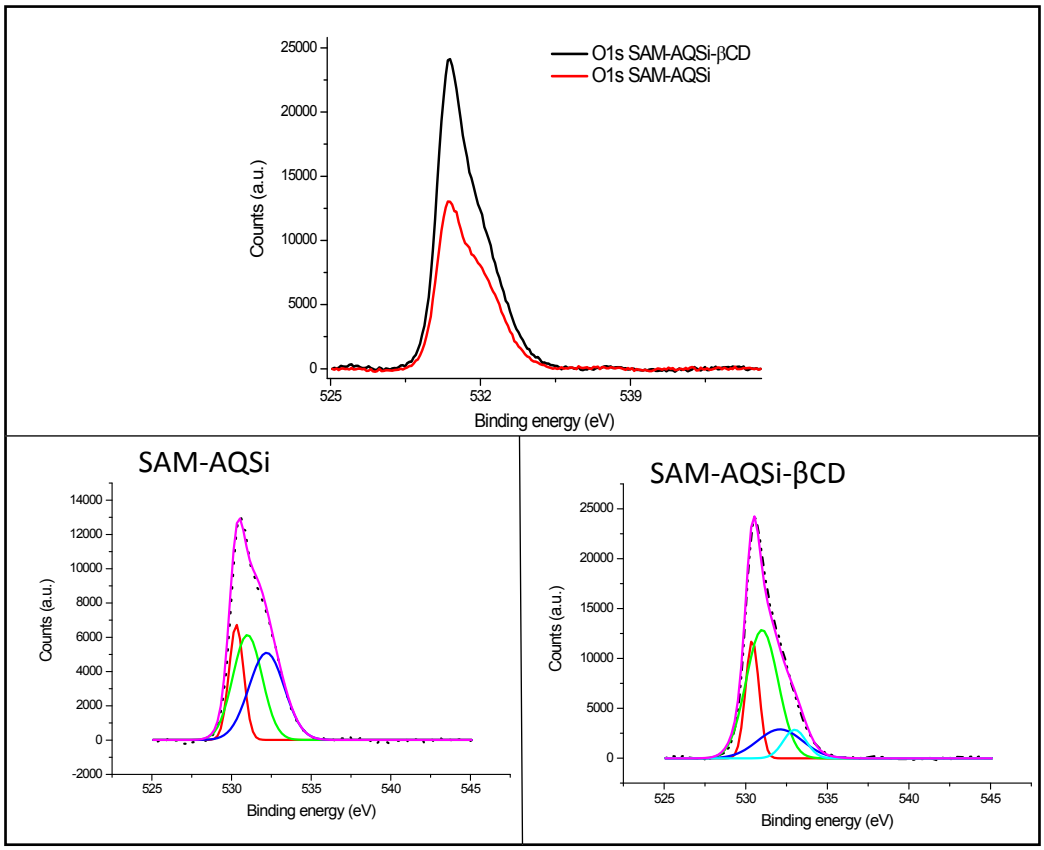


Figure S6: Study of the interaction between β-CD and the AQSi-SAM on ITO followed by cyclic voltammetry. The CV of AQSi-SAM was registred (black line). Then, the substrate was immersed in a 9 mM solution of β-CDs in ultrapure water during 3h. After that the substrate was washed with 50 mL of ultrapure water and dried under nitrogen stream. The CV was then registered again (red line). AQSi-SAM on ITO was used as the working electrode, a platinum wire as counter electrode and a silver wire as quasi-reference. A solution 0.1 M of NBu_4PF_6 in DCM:ACN (9:1) was used as electrolyte.



SAM-FcSH$_{dil}$		
Atom	**Binding energy (eV)**	**Type of bond**
C1s	284.8	**C**-C/**C**-H
S2p 3/2	161.9	**S**-Au
S2p1/2	163.1	**S**-Au
SAM FcSH$_{dil}$_βCD		
Atom	**Binding energy (eV)**	**Type of bond**
C1s	284.8; 286.8; 288	**C**-C/**C**-H; **C**-O; O-**C**-O;
O1s	533.2	**O**H; **O**-C-O
S2p3/2	161.9	**S**-Au
S2p1/2	163.1	**S**-Au

Figure S7: XPS analysis of FcSH$_{dil}$-SAM before and after the formation of the Host-Guest complex with β-CD.



SAM-AQSi		
Atom	**Binding energy (eV)**	**Type of bond**
C1s	283.9; 285.3; 287.9; 288.7	**C**-Si/C=C; **C**-C/**C**-H; O=**C**N/SiO-**C**; **C**=O
O1s	530.4; 531; 532.1	(metal oxide; Si-**O;** **C**=O)
Si2p	102.5	
SAM-AQSi_βCD		
Atom	**Binding energy (eV)**	**Type of bond**
C1s	283.8; 285.3; 286.8; 288.1; 288.8	**C**-Si/**C**=C; **C**-C/**C**-H; **C**-O; O-**C**-O; **C**=O
O1s	530.4; 531; 532.1; 533	Metal oxide; Si-**O**;C=**O**;**O**H/**O**-C-O
Si2p	102.5	

Figure S8: XPS analysis of AQSi-SAM before and after the formation of the Host-Guest complex with β-CD.

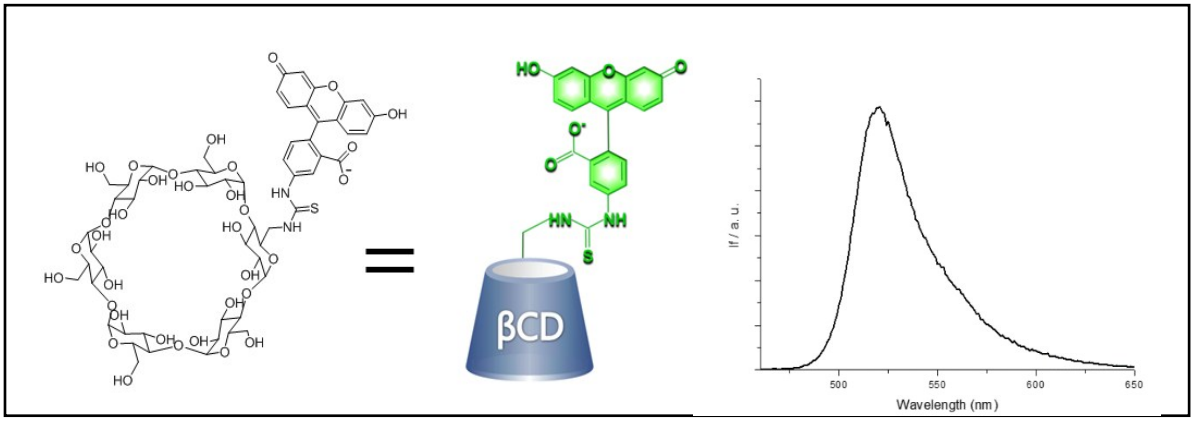


Figure S9: F-β-CD used and its emission spectrum (c=1% in water).

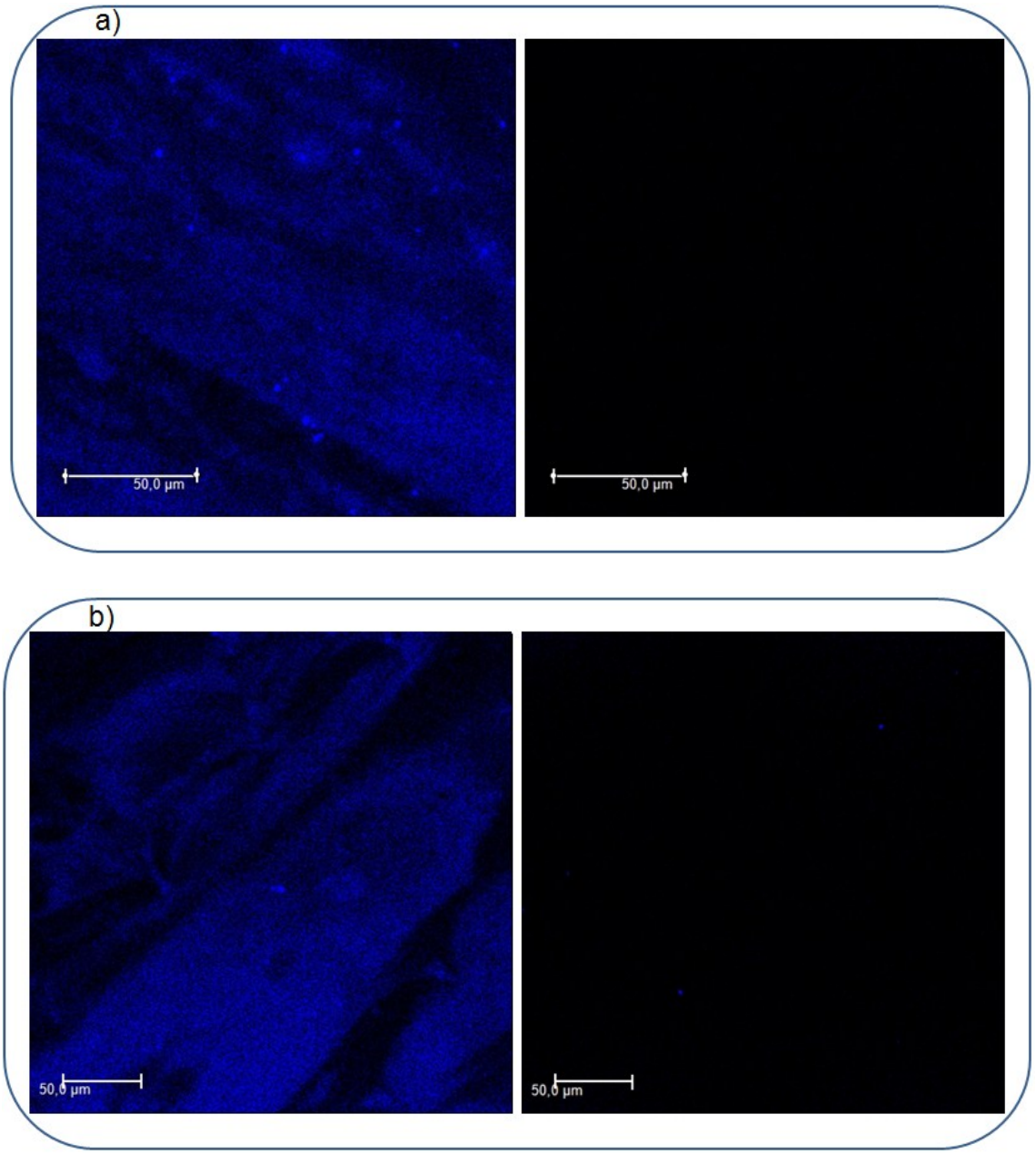


Figure S10: Confocal microscope images of a) $FcSH_{dil}$-SAM (left) and of a $C_{10}SH$ SAM (right) on Au and b) AQSi-SAM (left) and SAM-$C_{11}SiCl_3$ (rigth) on ITO, after the selective interaction with F-β-CDs. All substrates were immersed in a solution of F-β-CDs in ultrapure water during 3 h. Then the surfaces were washed with ultrapure water (50 mL) and dried under nitrogen flow.

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[i] P. Saint-Cricq, T. Pigot, Lionel Nicole, C. Sanchez and S. Lacombe, *Chem.Commun,* 2009, **0**, 5281.
[ii] J. Casado-Montenegro, E. Marchante, N. Crivillers, C. Rovira, and M. Mas-Torrent, *ChemPhysChem*, 2016, **17**, 1