Supporting Information

Surface Modification of Pseudoboehmite-Coated Aluminum Plates with Squaramic Acid Amphiphiles

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1. Materials and Methods

$^1$H NMR spectra (at 300 MHz) and $^{13}$C NMR spectra (at 75 MHz) were recorded on a 300 MHz Bruker AVANCE spectrometers in [D6]-DMSO solutions at room temperature. The residual proton signal was used as the reference. Chemical shifts ($\delta$) are given in ppm and coupling constants ($J$) in Hz.

*Atomic Force Microscopy.* The AFM images in tapping mode have been taken at room temperature and pressure using an AFM MultiMode Veeco microscope with a NanoScope IV controller. Silicone tips HQ: NSC35 / AlBS with a cantilever length of 90 μm have been used, operating in a frequency region of 150-300 kHz and a scanning ratio of 1.0 Hz. The electropolished aluminum samples used to obtain the images have been machined forming square pieces of 1 cm$^2$ of surface and 1 mm thick. These pieces have been placed directly in the microscope sample holder.

*Scanning electron microscopy.* The SEM images were obtained in a Hitachi S-3400N microscope with an acceleration voltage of 10 kV. The samples used to obtain these images, as for AFM, were square pieces of electropolished aluminum 1 cm$^2$ and 1 mm thick, located directly on the microscope sample holder.

*Mass spectra.* Mass spectra by MALDI-TOF have been acquired using an Autoflex spectrometer (Bruker). The aluminum plates functionalized with 1 have been coated with a matrix of 2,5-dihydroxybenzoic acid (DHB) and fixed to the sample plate using copper adhesive tape. Samples have been shot with a laser power of 60% (1000 shots). HRMS-ESI mass spectra were recorded on Thermo Scientific Orbitrap Q Exactive mass spectrometer equipped with electrospray modules.

*X-Ray Photoelectronic Spectroscopy (XPS).* XPS measurements were carried out in a SPECS system (Berlin, Germany) equipped with a Phoibos 150 1D-DLD analyzer and a monochromatic Al Kα radiation source (1486.7 eV). An initial analysis of the elements present was carried out (wide scan: energy step 1 eV, dwell time 0.1 s, energy pass 80 eV) and detailed analyses of the present elements were carried out (detail scan: energy step 0.1 eV, dwell time 0.1 s, energy pass 30 eV) with an electron exit angle of 90°. The
spectra were analyzed using the CasaXPS 2.3.16 software, which models the Gauss-Lorentzian contributions after the background subtraction (Shirley).

*Reflectance UV-Vis.* The total reflectance UV spectra were recorded in a Varian Cary 300Bio spectrophotometer provided with a DRA-CA-30I (Agilent) integrating sphere accessory (70 mm aperture diameter, LabSphere). The sample was placed in front of the aperture with an adapter wedge, so that the radiation is focused on the sample with an incidence angle of $8^\circ$. In this way, the total reflectance UV-vis spectrum is acquired as the sum of the specular and diffuse reflectance. A Spectralon® (PTFE) disc was used to record the blank. Spectralon® is the same material that covers the inside of the integrating sphere.

The DRA is an integrating sphere accessory that replaces the sample compartment of the spectrophotometer instrument. An integrating sphere is a hollow optical device, either constructed from or coated internally with a white diffusing material and fitted with the same detector configuration as the host spectrophotometer.

![Scheme S1](image_url)

**Scheme S1.** Scheme of the reflectance UV-Vis measurements.
2. Synthetic procedures

![Scheme S2. Synthetic route for 1-4.]

General procedure for the synthesis of compounds 1-4: a solution of 2 mmol of diethyl squarate in 10 mL of MeCN was added dropwise on a 2.2 mmol solution of the corresponding amine in 10 mL of MeCN under stirring. The mixture was stirred for additional 12 hours at room temperature. Then, the solution was concentrated and the resulting solid was refluxed for 12 h in 20 mL of water. The suspension was filtered and the solid subsequently washed with 1M NaOH (2×20mL), MeCN (2×20mL), CH₂Cl₂ (2×20mL), MeCN (2×20mL), 1M HCl (2×20mL) and MeCN (2×20mL). The solid was dried under vacuum to yield the corresponding squaramic acid as a white solid.

**3-hydroxy-4-(hexadecylamino)cyclobut-3-en-1,2-dione (1).**

Prepared following the general procedure. 340 mg (2 mmol) of diethyl squarate in 10 mL of MeCN, 470 mg (2.2 mmol) of hexadecylamine in 10 mL of MeCN. 555 mg of 1 (1.58 mmol), 79% yield.

**1H NMR (300 MHz, DMSO-d6, δ):** 8.37 (br s, 1H, NH), 3.36 (q, 2H, J = 6.6, CH₂), 1.49 (s, 2H, CH₂), 1.23 (s, 26H, CH₂), 0.85 (s, 3H, CH₃); **13C NMR (75 MHz, DMSO-d6, δ):** 194.64, 184.67, 173.98, 43.45, 31.27, 30.29, 29.01, 28.90, 28.68, 28.53, 25.78, 22.07 y 13.93; HRMS (ESI(-), m/z): [M]- calcld. for C₂₀H₃₄NO₃, 336.2544; found, 336.2542.

**3-hydroxy-4-(dodecylamino)cyclobut-3-en-1,2-dione (2).**

Prepared following the general procedure. 340 mg (2 mmol) of diethyl squarate in 10 mL of MeCN, 470 mg (2.2 mmol) of hexadecylamine in 10 mL of MeCN. 555 mg of 1 (1.58 mmol), 79% yield.

**1H NMR (300 MHz, DMSO-d6, δ):** 8.37 (br s, 1H, NH), 3.36 (q, 2H, J = 6.6, CH₂), 1.49 (s, 2H, CH₂), 1.23 (s, 26H, CH₂), 0.85 (s, 3H, CH₃); **13C NMR (75 MHz, DMSO-d6, δ):** 194.64, 184.67, 173.98, 43.45, 31.27, 30.29, 29.01, 28.90, 28.68, 28.53, 25.78, 22.07 y 13.93; HRMS (ESI(-), m/z): [M]- calcld. for C₂₀H₃₄NO₃, 336.2544; found, 336.2542.
25.77, 22.07 y 13.94; HRMS (ESI(-), m/z): [M]− calcd. for C_{16}H_{26}NO_{3}, 280.1918; found, 280.1907.

**3-hydroxy-4-(octylamino)cyclobut-3-en-1,2-dione (3).**
Prepared following the general procedure. 340 mg (2 mmol) of diethyl squarate in 10 mL of MeCN, 284 mg (2.2 mmol) of octylamine in 10 mL of MeCN. 320 mg of 3 (1.42 mmol), 71% yield.

1H NMR (300 MHz, DMSO-d6, δ): 8.39 (br s, 1H, NH), 3.49 (q, 2H, J = 6.6, CH₂), 1.50 (m, 2H, CH₂), 1.25 (s, 10H, CH₂), 0.85 (t, 3H, J = 7.0, CH₃); 13C NMR (75 MHz, DMSO-d6, δ): 184.54, 173.90, 43.44, 31.16, 30.26, 28.54, 28.47, 25.76, 22.03 y 13.91; HRMS (ESI(-), m/z): [M]− calcd. for C_{12}H_{18}NO_{3}, 224.1292; found, 224.1288.

**3-hydroxy-4-(butylaminocyclobut-3-en-1,2-dione (4).**
Prepared following the general procedure. 340 mg (2 mmol) of diethyl squarate in 10 mL of MeCN, 161 mg (2.2 mmol) of butylamine in 10 mL of MeCN. 308 mg of 4 (1.82 mmol), 91% yield.

1H NMR (300 MHz, DMSO-d6, δ): 8.40 (br s, 1H, NH), 3.38 (q, 2H, J = 6.6, CH₂), 1.49 (m, 2H, CH₂), 1.29 (m, 2H, CH₂), 0.87 (t, 3H, J = 7.0, CH₃); 13C NMR (75 MHz, DMSO-d6, δ): 192.10, 184.87, 174.37, 43.72, 32.91, 19.52, y 13.98; HRMS (ESI(-), m/z): [M]− calcd. for C₈H_{11}NO₃, 169.0739; found, 169.0731.
3. Atomic Force Microscopy (AFM) and SEM images

**Figure S1.** AFM images (a), the corresponding amplitude images (b), and the cross section profiles (c) (2×2 μm, z-axis scale: 200 nm) of aluminum plates functionalized with squaramic acids 4 (A), 3 (B), and 2 (C).

**Scanning electron microscopy (SEM)**

**Figure S2.** SEM images of aluminium samples before (A) and after (B) activation, and after adsorption of 1 (C) and PA (D), respectively. Scale bar: 1 μm.
4. MALDI-TOF

Figure S3. MALDI-TOF spectrum registered directly shooting on an aluminium plate functionalized with 1.
Figure S4. XPS spectra registered on aluminum plates, as received (black), after activation (AlOOH) (grey), and after functionalization with 1 (red).

Figure S5. Comparative histogram of percentages for the elements present on the surface of the aluminum samples. Aluminum: aluminum plates as received, Al(O)OH: aluminum plates after activation, Al(O)OH-1: aluminum plates functionalized with 1. The values were extracted from the relative total areas of the signals obtained by XPS spectra (Figure S4).
### 6. Grazing-Angle FT-IR (GA-FTIR)

**Table S1.** Assignment of IR bands corresponding to 1 and PA in adsorbed state and with KBr.

| chemical group  | vibrational type | Wavenumber (cm⁻¹) | 1 KBr | Adsorbed state | PA KBr | Adsorbed state |
|-----------------|------------------|--------------------|-------|----------------|--------|----------------|
| CH₃             | νₘ(C—H)          | 2951               | 2960  | 2955           | 2960   |
| CH₂             | νₘ(C—H)          | 2915               | 2926  | 2917           | 2926   |
| CH₂             | νₙ(C—H)          | 2850               | 2856  | 2849           | 2856   |
| cyclobutenedione | νₙ(breathing)    | 1817               | 1792  | -              | -      |

**Figure S6.** GA-IR spectra of different activated aluminium plates with increasing immersion times in a solution of 1 (left), and PA (right). The immersion times are indicated in the graph in hours. The grey IR spectra (KBr) correspond to the pure compound 1 (left), and PA (right).
7. UV Desorption Experiments

![Graph showing UV desorption experiments](image)

**Figure S7.** Evolution of the squaramic acid UV band 268 nm obtained by total reflectance UV-vis measurements throughout the process of desorption by immersion in isopropanol.
8. Theoretical Methods

The calculations of the noncovalent interactions and were carried out using the Gaussian-09 and the B3LYP/6-31G* level of theory. In order to generate the surface, geometry optimization of a bulk boehmite supercell of 100 atoms (γ-AlOOH) was performed starting from the experimental structure. The (010) surface, was selected since previous studies have already shown that is the most stable, and, moreover, it has been successfully used to analyze the insertion of phosphonic acids. From this optimized structure, several models were built, two for the squaramide derivative and two for the carboxylic acid (1:1 and 1:2 boehmite:squaramate/COOH stoichiometry), considering a monodentate adsorption mode.

![Figure S8. Optimized geometries for boehmite:squaramate (left) and boehmite:carboxylate (right) systems with 1:2 stoichiometries.](image)

The NCI plot is a visualization index that efficiently allows the identification and visualization of non-covalent interactions. It is based on the electron density and its derivatives and the isosurfaces correspond to both favorable and unfavorable interactions. They are easily differentiated by the sign of the second density Hessian eigenvalue and defined by the isosurface color. NCI analysis is a very convenient tool to rationalize host–guest complementarity and to know which interactions stabilize a complex. The color scheme is a red-yellow-green-blue scale with red for $\rho_{\text{cut}}^+$ (repulsive) and blue for $\rho_{\text{cut}}^-$ (attractive). Yellow and green surfaces correspond to weak repulsive and weak attractive interactions, respectively.
Figure S9. NCI plots of the boehmite:squaramate (left) and boehmite:carboxylate (right) with 1:2 stoichiometry.
9. $^1$H and $^{13}$C NMR spectra of the new compounds

Figure S10. $^1$H RMN spectrum in DMSO-$d_6$ of compound 1.
Figure S11. $^{13}$C RMN spectrum in DMSO-$d_6$ of compound 1.
Figure S12. $^1$H RMN spectrum in DMSO-$d_6$ of compound 2.
\( ^{13}\text{C} \) NMR, DMSO, 75 MHz, 298 K

**Figure S13.** \( ^{13}\text{C} \) RMN spectrum in DMSO-\( d_6 \) of compound 2.
Figure S14. $^1$H RMN spectrum in DMSO-$d_6$ of compound 3.
$^{13}$C NMR, DMSO, 75 MHz, 298 K

Figure S15. $^{13}$C RMN spectrum in DMSO-$d_6$ of compound 3.
10. References

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