

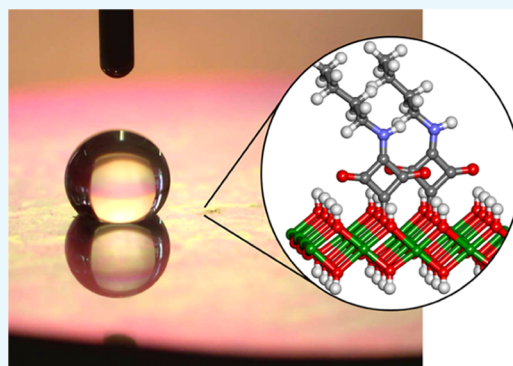
Surface Modification of Pseudoboehmite-Coated Aluminum Plates with Squaramic Acid Amphiphiles

Carlos López, Bartomeu Galmés, Bartolomé Soberats,^{1b} Antonio Frontera,^{1b} Carmen Rotger, and Antonio Costa*^{1b}

Department of Chemistry, Universitat de les Illes Balears, Ctra. Valldemossa km 7.5, 07122 Palma, Spain

S Supporting Information

ABSTRACT: The functionalization of interfaces has become very important for the protection or modification of metal (metal oxides) surfaces. The functionalization of aluminum is particularly interesting because of its relevance in fabricating components for electronic devices. In this work, the utilization of squaramic acids for the functionalization of aluminum substrates is reported for the first time. The physicochemical properties of the interfaces rendered by *n*-alkyl squaramic acids on aluminum metal substrates coated with pseudoboehmite [Al(O)_x(OH)_y] layers are characterized by contact angle, grazing-angle Fourier-transform infrared spectroscopy, atomic force microscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, and matrix-assisted laser desorption ionization time-of-flight. Moreover, we could confirm the squaramic functionalization of the substrates by diffuse reflectance UV–vis spectroscopy, which cannot be used for the characterization of UV–vis-inactive substrates such as carboxylates and phosphonates, commonly used for coating metallic surfaces. Remarkably, the results of sorption experiments indicate that long-chain alkyl squaramic acid desorbs from activated-aluminum substrates at a reduced rate compared to palmitic acid, a carboxylic acid frequently used for the functionalization of metal oxide surfaces. Theoretical calculations indicate that the improved anchoring properties of squaramic acids over carboxylates are probably due to the formation of additional hydrogen bonding interactions on the interface. Accordingly, we propose *N*-alkyl squaramic acids as new moieties for efficient functionalization of metal oxides.



INTRODUCTION

Squaramides, the 3,4-diaminoderivatives of squaric acid,^{1,2} have received increasing attention during recent years because of their broad range of applications in many fields such as ion recognition and transport,^{3–7} sensing,^{8–10} catalysis,^{11,12} biomedicine,^{5,13,14} and material science.^{15–17} Squaramides are planar and aromatic compounds with two carbonyl and two amide-type NH groups which make these molecules suitable for strong hydrogen bonding interactions (Figure 1a).¹ Indeed, squaramides exhibit unique association abilities via hydrogen bonding and stacking interactions, which is the basis of their chemistry. Less known 3-hydroxy-4-amino derivatives

of squaric acid, referred to henceforth as squaramic acids (Figure 1b), combine in its molecular structure acidic OH and amide-type NH groups suitable for providing ionic and hydrogen bonding interactions.^{17–19} Squaramic acids exhibit very high kinetic stabilities with pK_a values at around 1–2, which ensure that they are deprotonated in a wide range of pH.^{18,19} Considering their oxoanionic structure and acid–base properties, we envisaged that squaramic acids could be used in applications that require acidic moieties while additional hydrogen bonding interactions could be beneficial to reinforce the binding of squaramic acids to solid surfaces. In this regard, it is well known that alkyl carboxylates and phosphonates, among others, can establish relatively strong interactions with oxide-based surfaces and nanoparticles.^{20–22} For example, treatment of metal oxide substrates with *n*-alkyl carboxylic acids leads to the adsorption of the organic molecules on the metal surface, which can also lead to the formation of self-assembled monolayers when surfactants (with long hydrocarbon chains) are used.^{23–26} This process is utilized to protect metals and oxides from erosion or decomposition and

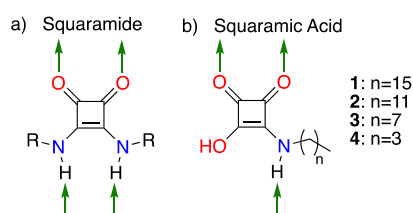


Figure 1. (a) Molecular structures of a bis-secondary squaramide and (b) squaramic acids 1–4. Putative hydrogen bonding interactions are indicated with green arrows.

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undesired chemical reactions and to provide additional properties (i.e., hydrophobic behavior), and therefore it is highly relevant for the material's development.^{27–29} It is generally accepted that these compounds are attached to the surface by the coordination of the oxoanionic groups to the metal oxide but depending on the conditions in the adjacent solution those bonds can be easily hydrolyzed.^{21,23,30–35} Thus, the reinforcement of those coordination bonds to avoid detachment of the functional groups is of high interest. In this direction, squaramic acids are highly acidic oxoanionic compounds with enhanced kinetic stability of the amide-type group toward hydrolytic degradation¹⁸ ideally suited to be used as anchoring moieties for the functionalization of metal oxide surfaces. Remarkably, they may be suitable to interact by a primary interaction between the oxoanionic groups of metal oxide surfaces, as per example aluminum oxide-hydroxide surface, and establish additional hydrogen bonding interactions (with the surface and with other squaramic moieties) utilizing the amide-type NH or the non-coordinated carbonyl groups. Accordingly, squaramic acids would be advantageous over carboxylic and phosphonic acids because they may be capable to establish multiple interactions at the interface of hydrophilic surfaces which may result in a strengthened linkage.

Herein, we report on the utilization of *N*-alkyl substituted squaramic acids 1–4 (Figure 1b) for the functionalization of metal aluminum substrates. Aluminum is a relevant material because of its extensive use in microelectronics,^{36–38} and therefore its functionalization is important for many applications. In the present work, the functionalization of the aluminum substrates was achieved after a previous thermal treatment with water, which produced an activated layer of aluminum oxyhydroxide, suitable for anchoring oxoanionic groups.^{31,34,39} The activated substrates treated with compounds 1–2 (bearing longer hydrocarbon chains) exhibit hydrophobic characteristics as it is deduced from water droplet–surface contact angles around 120° (Figure 2). The

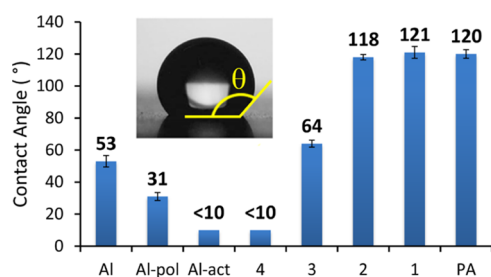


Figure 2. Contact angle values (θ) of the different aluminum substrates before and after functionalization with squaramic acids 1–4 and PA, respectively. Inset image shows the representation of the calculation of the contact angle of a water droplet on the surface. Al: aluminum plates as received, Al-pol: aluminum plates after polishing; Al-act: aluminum plates after activation with boiling water. The contact angles of the plates functionalized with the different acids are indicated with the corresponding code number of the squaramic acid (Figure 1b).

attachment of squaramic acid groups on the surface is demonstrated and characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF), grazing-angle Fourier-transform infrared spectroscopy (GA-FTIR), and diffuse reflectance UV measurements. Remarkably, desorption experi-

ments and theoretical calculations reveal that squaramic acid 1 binds more strongly on the activated aluminum surfaces than palmitic acid (PA), a compound commonly used for surface modification. Accordingly, squaramic acid motifs are candidates to be used for the functionalization of metal oxide surfaces with reinforced interactions.

RESULTS AND DISCUSSION

Compounds 1–4 were prepared via a straightforward synthetic procedure from the corresponding alkylamine and diethyl squarate (see Experimental Section and Supporting Information). In the first step, diethyl squarate was allowed to react in acetonitrile with one equivalent of the selected alkyl amine to produce the mixed squaramide ester. After solvent evaporation, the residue was treated with boiling water to produce the corresponding squaramic acid with moderate-to-good yields. Accordingly, the final squaramic acids were obtained via an easy synthetic method, easy work-up and from commercially available compounds.

For the functionalization of aluminum plates with squaramic acids, the plates were first polished and then activated by treatment with boiling water, according to a previously described procedure (see Experimental Section).³² This process produces an aluminum oxyhydroxide (with a pseudoboehmite structure)^{36,37} thin film on the surface, enabling the substrate to be used in adsorption experiments.³² The coordination of carboxylic acids to alumina derivatives is well-known,^{42–46} and we expected that squaramic derivatives could coordinate pseudo-boehmite interfaces in a similar mode. The activated substrates were subsequently treated with the selected squaramic acid 1–4 suspended in heptane (see Experimental Section). The hydrophobicity of the already deposited material, indicative of the attachment of the organic compounds, was tested by contact angle measurements (Figure 2 inset and Experimental Section). Figure 2 indicates the contact angles of different aluminum substrates before and after the treatment with PA and the squaramic acids 1–4 compared to that for PA taken as reference.

The commercial aluminum plates show contact angles of around 53° but decrease to 31° after the polishing process. The subsequent hydrothermal activation gives rise to contact angles below 10°.³² These results indicate the high hydrophilicity of the surface after the activation process, which is consistent with the formation of an aluminum oxy-hydroxide layer.^{40,41} As expected, the contact angles drastically increase after the treatment of the activated plates with squaric acids 1–3, while remains below 10° for the plates soaked with 4. The larger contact angles were observed for the substrates treated with squaramic acids 1 (121°) and 2 (118°) with longer alkyl chains. These results are consistent with the successful adsorption of the squaramic acids on the surface, where the polar parts interact with the aluminum oxy-hydroxide interface and the alkyl chains are perpendicular to the surface in contact to air. Accordingly, the derivatives with longer alkyl groups namely, hexadecyl and dodecyl, provide higher hydrophobic character of the substrates.²¹ The higher ability of long hydrocarbon chains to form self-assembled monolayers could also play a role in the increased hydrophobicity.^{23–26} As control experiments, activated aluminum plates were treated with PA, following the analogous procedure utilized for 1–4 (see Experimental Section). The substrate treated with PA showed contact angles (120°) similar to the plates treated with squaramic acid 1 (121°) with analogous hydrocarbon chain.

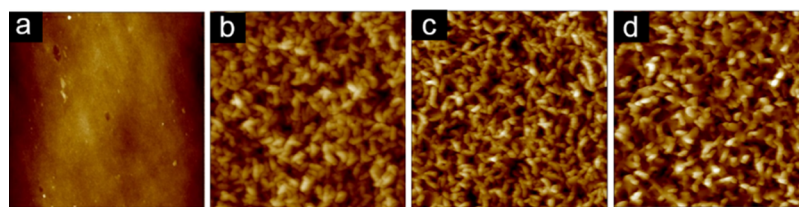


Figure 3. Surface topographic AFM images ($2 \times 2 \mu\text{m}$): (a) Polished aluminum surface. (b) Neat activated aluminum surface before (b) and after deposition of **1** (c) or PA (d) on the activated aluminum surface.

Those contact angles are lower than that measured in superhydrophobic surfaces prepared by coating-functionalized alumina nanoparticles (155°),⁴⁷ but they are consistent with a regular functionalization of the surfaces by SAMs.^{23,26}

To get insight into the characteristics of the functionalized aluminum plates, we analyzed the changes experienced by the aluminum plates after the treatment with squaramic acid **1** by AFM and SEM (Figure 3 and Figures S1 and S2). Both microscopic techniques provided similar results. After polishing, AFM images show a smooth surface of the metallic plates (Figure 3a). However, after the activation with boiling water, the aluminum surface becomes altered due to the formation of a pseudoboehmite oxide hydroxide layer.^{31,48} Figure 3b shows the AFM image of the activated aluminum surface where randomly distributed wormlike nanostructures can be appreciated. This uniform pattern, as well as the corresponding cross-section profiles, appears unaltered after the treatment with **1** or PA (Figures 3c,d). Accordingly, both contact angle and AFM experiments indicate that the squaramic acid **1** or PA attaches to the aluminum surface without extensive multilayer deposition, which would lead to an increase of the thickness of the cross-section and a decrease of the surface roughness.

Mass spectrometry (MALDI-TOF), XPS, UV-vis reflectance spectroscopy, and GA-FTIR experiments (see Experimental Section and Supporting Information) support the attachment of squaramic acid **1** on the activated aluminum surfaces. MALDI-TOF experiments performed by directly shooting on the aluminum substrates treated with compound **1** showed two peaks at 338.477 and 360.462 m/z assigned to $(M + H)^+$ and $(M + Na)^+$, respectively (Figure S3). In the same vein, XPS shows a chemical composition on the surface of 0.9% of N, 22.8% of C, 53.7% of oxygen, and 22.6% of Al. This composition is consistent with the presence of squaramic acid **1** on the substrate (Figures S4 and S5). Furthermore, the attachment of **1** on the substrates was monitored by total reflectance UV experiments because squaramic acids, unlike other common chemical groups used for these purposes such as *n*-alkyl carboxylic acids or phosphonic acids, are UV-active compounds. The UV-vis reflectance spectrum of an aluminum substrate functionalized with **1** shows an intense and broad peak with a maximum located at around 268 nm (Figure 4) assigned to “HOMO–LUMO” transition of the squaryl group. This band compares with the absorption profile of squaramic acid **4**, the only water-soluble squaramic acid presented in this work¹⁹ (Figure 4 inset). Remarkably, the use of reflectance UV-vis experiments has never been applied for this purpose because *n*-alkyl carboxylic acids or phosphonic acids typically used for these purposes do not exhibit suitable absorption features.

GA-FTIR experiments were also carried out to get insight into the strength of the attachment of the squaramic acid **1** with the activated aluminum plates. Figure 5 shows the

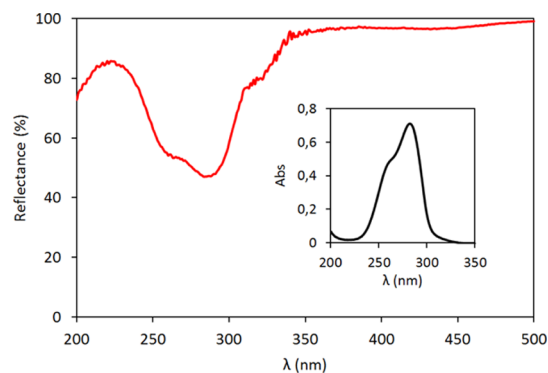


Figure 4. Total reflectance spectra in the UV-vis region of an aluminum plate functionalized with **1**. Inset: Absorbance spectrum of **4** ($2.0 \times 10^{-5} \text{ M}$) in water.

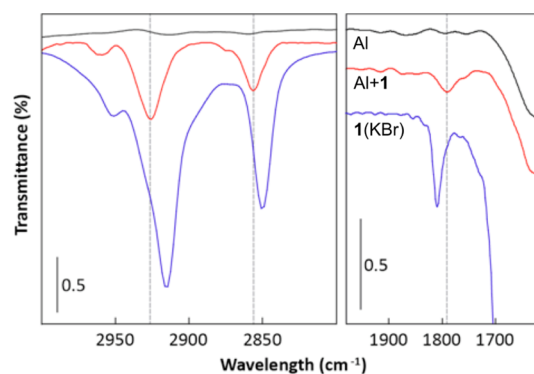


Figure 5. Relevant parts of the GA-FTIR spectrum of the activated aluminum plates before (black) and after (red) functionalization with squaramic acid **1**. Relevant parts of the FTIR spectrum of compound **1** in KBr (blue).

relevant areas of the IR spectra of **1** in KBr and the activated aluminum plates before and after the treatment with **1**. Aluminum plates treated with **1** show absorption bands associated with C–H stretching vibrations of the *n*-alkyl chain at 2800–3000 and the diagnostic breathing band of the squaryl moiety at around 1800 cm^{-1} (Figure 5). Specifically, the C–H stretching vibrations of **1** appear at 2951, 2915, and 2850 cm^{-1} and the characteristic breathing band of the cyclobutenedione moiety at 1817 cm^{-1} when measured as unionized squaramic acid in KBr. These frequencies change to 2960, 2926, 2856, and 1792 cm^{-1} , respectively, when **1** is adsorbed on the aluminum plates (Figure 5 and Table S1). The shift of the breathing band from 1817 to 1792 cm^{-1} suggests the presence of squaramate anions interacting with the aluminum surface⁴⁹ and is in accordance with coordination models previously proposed for carboxylates and phosphonates.²¹ Unfortunately, not much information of other vibrations (i.e. NH) can be

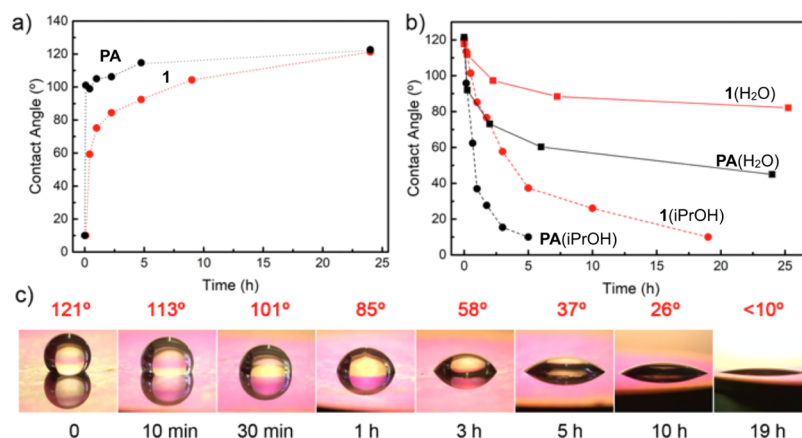


Figure 6. (a) Plot of the contact angles measured by treating activated aluminum plates with solutions of PA (black circles) and 1 (red circles) in heptane as a function of the immersion period. (b) Contact angles of the fully functionalized plates with PA (black) and 1 (red) immersed in water (squares) or iPrOH (circles) for increasing periods. (c) Side views of a sessile drop on the aluminum substrates fully functionalized with 1 and immersed in isopropanol for different periods. The corresponding contact angle values and the immersion times are indicated above and below each image, respectively.

traced from these experiments because of the low resolution of the technique. The attachment of PA on the substrates was also monitored by GA-FTIR, but in this case only the signals corresponding to the stretching of the hydrocarbon chains were observed (Figure S6 and Table S1).

To evaluate the strength of the attachment of the squaramic acids on the activated alumina surfaces, we performed adsorption/desorption experiments of 1 and PA. The adsorption experiments were carried out on activated aluminum plates immersed in a solution of 1 or PA in heptane for increasing periods. Then, the plates were analyzed by GA-FTIR and contact angle measurements. Figure 6a shows a representation of the contact angles of aluminum plates treated with PA and 1 for different immersion periods. In both cases, longer immersion leads to an increase of the water–substrates contact angles. These results, which are according to GA-FTIR experiments (Figure S6), are attributed to an increase of the adsorbed organic compound. Under these experimental conditions, it is apparent that the adsorption of PA is faster than with 1, which is probably related to the better solubility of PA in the heptane media. While the adsorption of PA reaches 80% of the maximum contact angle in 5 min, compound 1 requires 8–9 h to reach similar values (Figure 6a). In both cases, no changes on the contact angles were observed for films immersed more than 24 h, which indicates that after this time the aluminum surface becomes saturated with the adsorbate.

Desorption of PA and 1 from the substrates was also evaluated by immersing the already functionalized aluminum plates (prepared by 24 h immersion in solutions of PA or 1) into isopropanol (iPrOH) or water. Isopropanol was chosen for the experiments because both acids are soluble in this solvent, while the experiments in water give us information about the robustness of the attachments of the molecules to the surfaces, which is useful to analyze their further application as coatings. It can be seen that, when the plates were immersed in iPrOH, the contact angles of the coated samples decrease by increasing the time of immersion (Figure 6b). It is noteworthy that the plates treated with PA requires 8 h of immersion to reach angles below 10°, while the plates treated with squaramic acid 1 requires 19 h. The decrease of the contact angles is associated with desorption of the organic compounds from the

surface, which is also confirmed by total reflectance UV experiments for plates treated with 1 (Figure S7). Thus, the desorption rate in iPrOH is slower with 1 than with PA-functionalized plates. Immersion in water led to a similar conclusion. Figure 6b shows a plot of the contact angles of the substrates coated with PA and 1 after different immersion periods in water. It is apparent that the desorption of plates coated with 1 is slower than with those treated with PA. The plates functionalized with PA decrease the contact angle below 50° after 24 h of immersion, while the plates treated with squaramic acid 1 decrease the contact angle only up to 80° with the same immersion times. Similar values were recorded after 48 h of immersion. From these experiments, it can be concluded that, as expected, adsorption of these compounds on activated aluminum is reversible due to the establishment of relatively weak interactions between the coating molecules and the aluminum substrates. However, it is clear that the kinetics of desorption of compound 1 from the aluminum plates is slower than for PA, which is an advantage to create more robust functionalization of surfaces.

We have carried out theoretical calculations (density functional theory) to investigate the mechanism of insertion of squaramate into the activated aluminum. For this purpose, a boehmite (γ -AlOOH) surface (100-atoms supercell) was generated and optimized (see Supporting Information for computational details). The resulting supercell displays OH groups on the surface, which are directly attached to the Al (octahedral geometry) atoms. The (010) surface was selected because previous studies have already shown that it is the most stable,⁵⁰ and, moreover, it has been successfully used to analyze the insertion of phosphonic acids.⁵¹ The proposed mechanism involves the protonation of one of the OH groups of the supercell by the squaramic acid (or carboxylic acid) and a subsequent replacement of water by the squaramate (or a carboxylate) anion through a coordination bond to two Al-atoms. For the theoretical studies, we have used squaramic acid 4 and butyric acid as models. The inserted complexes were optimized at the B3LYP/6-31G* level of theory, and it was found that the most stable coordination mode for squaramate is through the central carbonyl group as it is shown in Figure 7a. Remarkably, this coordination mode provides two hydrogen bonding interactions between the two carbonyls of the

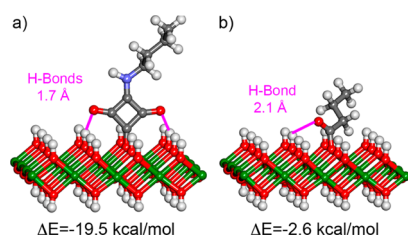


Figure 7. Optimization geometries (B3LYP/6-31G*) of the system based on a boehmite (γ -AlOOH) supercell and (a) squaramate and (b) carboxylate anions.

squaramate and two vicinal OH groups of the boehmite surface (OH \cdots OC distance of 1.70 Å and O–H \cdots O angle 153°). This coordination mode presents a binding energy of -19.5 kcal/mol, which corresponds to the replacement of an OH $^-$ by the squaramate with the concomitant release of a water molecule. In contrast, the boehmite–carboxylate system presents significantly reduced binding energy (-2.6 kcal/mol, see Figure 7b), where only one hydrogen bond is formed, which exhibits longer OH \cdots OC distance (2.13 Å) compared to the squaramate and a very poor directionality (O–H \cdots O angle is 119°). We have further analyzed and described in the Supporting Information the effect of the insertion of a second squaramate or carboxylate moiety (see Figure S8). In short, the insertion of the second squarate provides an extra stabilization energy of 3.4 kcal/mol due to an antiparallel CO \cdots CO interaction (Figure S9), while the insertion of a second carboxylate does not. These results agree with the desorption experiments.

CONCLUSIONS

In summary, we have shown that squaramic acid is a suitable moiety for the functionalization of activated aluminum surfaces. The synthesis of these compounds is easy and can be prepared in a large scale in only one-step synthesis from commercially available compounds, which make these compounds suitable for industrial applications. It was demonstrated that squaramic acid **1** physically adsorbs on aluminum oxy-hydroxide layer forming a hydrophobic monolayer on the surface. Remarkably, desorption of **1** from the aluminum surface in isopropanol is slower than for **PA**, suggesting the formation of a stronger attachment by using squaramic acid. Theoretical calculations indicate that the reinforced squaramic–substrate interactions are due to the formation of hydrogen bonding interactions, enabled due to the unique molecular structure of squaramate anions with three accepting C–O groups. Accordingly, squaramic acids are serious candidates to be applied in the functionalization of metal oxides offering improved attachment properties compared to carboxylic acids.

EXPERIMENTAL SECTION

Materials and Solutions. All the chemicals and reagents were of commercial origin (Aldrich or Scharlau) and were used as received. All the solvents were purchased from Scharlau. The deuterated solvents for the NMR studies were purchased from Euriso-top. The aluminum plates used for the experiments are based on polycrystalline aluminum (Al 99.99%, Si 0.01%) of 1 mm thickness and were purchased from ABCR (Germany). Two types of plates were used, squares of 1 × 1

cm for the AFM experiments and disks of 2.5 cm 2 for the rest of the experiments.

General Synthesis of Squaramic Acids 1–4. Diethyl squarate (340 mg, 2 mmol) in 10 mL of MeCN was added dropwise to a 2.2 mmol solution of the corresponding amine in 10 mL of MeCN under stirring. The mixture was left for 12 h under stirring 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 was subsequently washed with 1 M NaOH (2 × 20 mL), MeCN (2 × 20 mL), CH $_2$ Cl $_2$ (2 × 20 mL), MeCN (2 × 20 mL), 1 M HCl (2 × 20 mL), and MeCN (2 × 20 mL). The remaining solid was dried under vacuum to yield the corresponding squaramic acid as a white amorphous solid. A detailed characterization of compounds 1–4 is described in the Supporting Information.

Activation of the Aluminum Substrates (Formation of Aluminum Oxyhydroxide Layer).

The aluminum substrates were activated following a previously described methodology.³² The square (1 × 1 cm) plates were polished via an electrolytic process by using a TenuPol-5 (Struers) apparatus [5 °C, 40 V, HClO $_4$ (60%)]. The disklike (2.5 cm 2) plates were mechanically polished by using successively SiC paper (#600 and #1200 grain size) and diamond particle suspensions (3 and 1 μ m, Buehler). After the polishing process, the plates were ultrasonicated for 2 min in an ethanol/water (1:1) mixture and then dried in an argon stream. The plates were then immersed in boiling water for 10 min and dried again in an argon stream.

Adsorption of Compounds 1–4 and PA. The adsorption of compounds 1–4 and **PA** on the aluminum plates was carried out immediately after the activation of the plates. The adsorption of **PA** was carried out by immersing the activated plates into a 0.05 mM solution in heptane for 24 h under orbital stirring. For the functionalization with compounds 1–4, the activated aluminum plates were immersed in a saturated solution of the corresponding acid, containing part as undissolved solid, (0.017 g/L) in heptane for 24 h under orbital stirring. Before the immersion of the plates, the initial milky suspension of the squaramic acid was ultrasonicated with a GEX 130 apparatus (Sonics) in the corresponding volume of heptane at 130 W for 10 min and filtered to remove insolubles. After the treatment with the acids, all the plates were immersed in a heptane solution and stirred (orbital) for 10 min and then dried in an argon stream. The plates treated with compounds 1–4 were additionally immersed into isopropanol and sonicated for 10 s to remove loosely adsorbed material and then dried under argon.

Adsorption and Desorption Experiments. For adsorption experiments, the plates were activated and immersed for different periods into the acid solution (**PA**) or (**1**) in heptane under orbital stirring. Then, the plates were washed and dried according to the previously described methodologies and used for the measurements. For desorption experiments, various plates were functionalized with **PA** or **1** following the general methodology. The resulting plates were immersed for variable periods ranging from 1 min to 24 h into isopropanol or water (20 mL) under orbital stirring. The plates were then dried in an argon stream and then used for the measurements.

Contact Angle Measurements. Static water contact angles were measured at room temperature using a homemade device equipped with a DinoXcope camera and using the sessile drop method and image analysis of a drop profile with

the software ImageJ. The volume of the water (Milli-Q) droplet was 5 μL . The contact angle values given here correspond to the average of three droplets.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01459.

Supporting experimental section including materials and the preparation of the squaramic acids; AFM and SEM images; MALDI-TOF data; XPS spectra; GA-FTIR data; UV desorption experiments; theoretical methods; and ^1H and ^{13}C NMR spectra of the new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: antoni.costa@uib.es.

ORCID

Bartolomé Soberats: 0000-0003-2128-6602

Antonio Frontera: 0000-0001-7840-2139

Antonio Costa: 0000-0002-9418-7798

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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