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ARTICLE

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Self-assembling of amino-terminated monolayers depending of the chemical structure

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Amino-terminated Self-Assembled Monolayers (SAMs) are widely used to functionalize silica surfaces as a primary layer in the field of biosensors. The use of commercial aminosilanes suffers from a lack of control of molecular organization due to the multiple interactions of the amine end group of the silylated coupling agent with the polar groups available on the surface and from the possible hydrolytic degradation of the layer. In this study, we report the successful preparation of well-defined amino-terminated monolayers obtained by a direct grafting strategy using phthalimide as a protected amino group to prevent undesirable non-covalent interactions. Three phthalimide-terminated silanes were synthesized for this purpose. Their grafting was achieved using the classic immersion method and the spincoating process. Polarization modulation infrared reflection-absorption spectroscopy (PM-IRRAS) was used to study the grafting efficiency and the phthalimide-terminated SAM organization. After the total conversion of the phthalimide into amine groups, the reactivity of the resulting amino-terminated monolayers was evaluated using a coumarin derivative as a fluorescent probe. The PM-IRRAS and the fluorescence measurements confirmed the reactivity of amino-terminated SAMs.

1. Introduction

SAMs are widely used as primary layer in the field of biosensors¹ and organic (bio)electronic^{2,3} applications to functionalize the surface of materials. Silane-based SAMs have been used extensively to modify silica surfaces and introduce specific functional terminal groups depending on the final applications.^{4,5} Amino-terminated SAMs prepared from commercially available silanes such as 3-aminopropyltriethoxysilane (APTES) and 3-aminopropyltrimethoxysilane (APTMS) are the most used to promote the biofunctionalization of a solid support in bioanalytical platforms,⁶ to study protein or cell adhesion⁷, or to functionalize (nano)particles.^{8,9,10} The formation of the aminosilane layer is sensitive to the reaction conditions, and the quality of the APTES or APTMS films depends on different parameters such as concentration,¹¹ nature of the solvent,¹² time,¹³ temperature,¹⁴ humidity level,¹⁵ and the post-deposition treatment (annealing step).^{16,17} Many experimental conditions were described to deposit aminosilane films by wet chemistry, giving rise to monolayer^{18,19} or multilayers²⁰ films.

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These trialkoxysilanes form siloxane bonds with the free surface hydroxyl groups and between neighboring silanes (horizontal polymerization). This enables silane polymerization in solution and leads to a topographic heterogeneity in terms of the flatness and uniformity of the aminosilane coatings, which can influence the applications.²¹ The uncontrolled layer structure is also responsible for a lack of reproducibility.²²

The molecular structure of the aminosilane influences the stability of the layer. The amino group of silane is able to catalyze the siloxane bond formation and hydrolysis. The short aminoalkyl silane (APTES) shows hydrolytic degradation upon exposure to water which promotes an extensive loss of molecules at the surface. This can be explained by the formation of a stable five-membered ring intermediate for intramolecular catalysis.²³ However increasing the length of the alkyl chain minimizes the amine catalyzed detachment and provides a hydrophobic spacer which prevents water penetration into the layer.^{24,25} In addition, the amino group impacts the molecular organization of the monolayer and the structure is difficult to control due to the multiple possibilities of interactions of the amino end group by hydrogen bonds and by electrostatic attractions. The ionic species and hydrogen bonds of amino groups promote disordered state, which can affect its accessibility and reactivity.^{18,26} Neutral amines are oriented away from the surface for biomolecule immobilization,²⁷ whereas the ionic species and hydrogen bonds are close to the surface.^{14,16,19,28} The APTES films prepared in anhydrous toluene exhibit more reactive surface amino groups than those obtained in aqueous solutions for the same reaction time.²⁹ When the propyl linker is replaced by the phenyl rigid linker which limits multiple orientations, the primary amine content reached 100% with more uniform film.¹⁸

To overcome the uncontrolled orientation of the aminosilane, a protecting group can be used to avoid the multiple interaction possibilities.^{30,31,32,33,34} The alkyl chain length can also affect the molecular self-assembly by van der Waals interactions in the monolayer. *N*-phthalimide protected aminosilanes form disordered monolayer with a C17 alkyl chain, whereas an ordered monolayer was obtained with a C21 alkyl chain.³⁵ Another strategy using the post-modification of the bromo-alkyl monolayer to amine group conversion via SN2 bromine-to-azide reactions provides a densely packed and organized monolayer.^{36,37}

The immersion solution^{25,38} and the chemical vapor deposition^{39,40} are the most widely used deposition processes to prepare aminosilane films onto a silica substrate. However, a few studies used spin coating^{41,42} or dipcoating⁴³ process. Recently, we have demonstrated that the spin coating process is an alternative way to prepare azide-terminated monolayers compared to the classical immersion solution.^{44,45} The spin coating process is fast, simple, easy to handle, conducted in ambient conditions and uses less amount of organic solvent whereas the immersion method takes several hours and uses more solvent in anhydrous conditions.

In this work, we explore the preparation of amino-terminated SAMs by the classical immersion method and the spin coating process. Three *N*-phthalimide protected aminosilanes were synthesized by varying the nature of the spacer between the end group and the trimethoxysilyl anchoring group. Phthalimide coupling agents with an alkyl chain as a spacer, as well as carbamate or urea groups inside the alkyl chain were studied. The silylated coupling agents bearing urea or carbamate groups were used to provide functionalized hydrogen-bonding SAMs.^{46,47,48,49}

In this paper, we investigate the influence of the structure of the organosilanes on monolayers organization and the method used to prepare the amino-terminated SAMs. The reactivity of the terminal

amine was evaluated by using a coupling reaction with a fluorescent probe. The corresponding phthalimide or amino-terminated SAMs have been characterized by Polarization Modulation Infrared Reflection-Absorption Spectroscopy (PM-IRRAS), Atomic Force Microscopy (AFM), wettability measurements and fluorescence spectroscopy.

2. Experimental

2.1. Synthesis of silylated coupling agents

The experimental procedures and characterizations of silylated coupling agents Si-Carba-Pht, Si-Urea-Pht, Si-Alk-Pht (scheme 1) as well as intermediate organic compounds are reported in details in the supporting information.

2.2. Materials and substrates

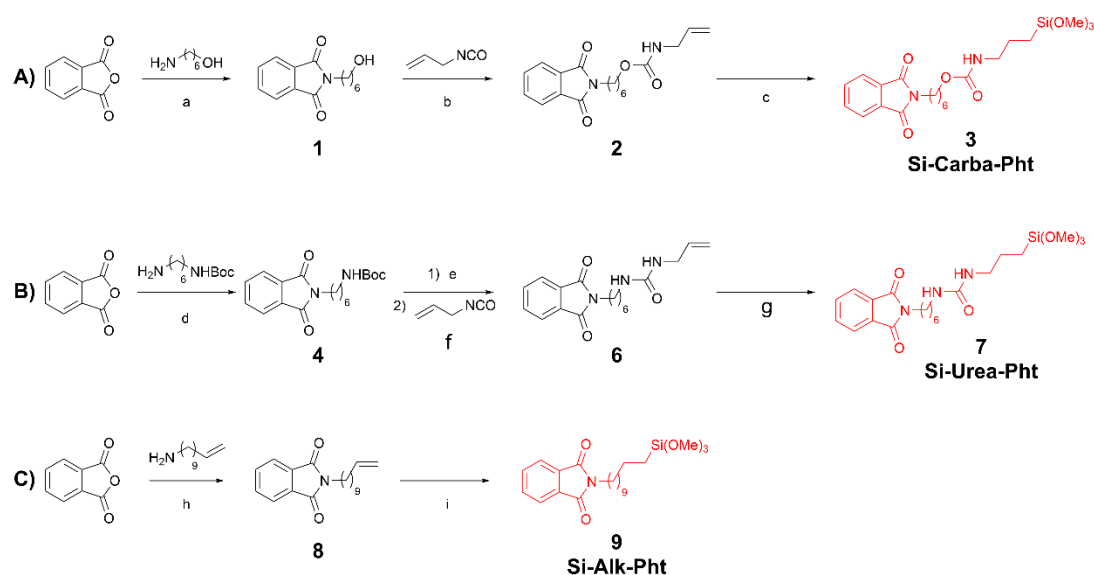
For PM-IRRAS experiments, SiO₂/Au substrates corresponding to Goldflex mirror with SiO₂ protection layer (Goldflex PRO, reference 200785), supplied by Optics Balzers AG, were used with a rms roughness of 0.9 nm.⁵⁰

2.3. Preparation of SAMs

Substrate cleaning procedure: Before grafting, the SiO₂/Au substrates were intensively washed with Milli-Q water (18 MΩ cm), sonicated for 15 min in chloroform and exposed to UV–ozone (185 – 254 nm) for 30 min. They were immediately used for silanization by the spin coating process or the immersion solution method.

Formation of phthalimide -terminated SAMs by the immersion method (iSAM): A solution of freshly prepared organosilane (0.05 mmol) in dry solvent (50 mL) was prepared in a schlenk flask under argon atmosphere. A solution of trichloroacetic acid (TCA) (0.8 mg, 5.10⁻⁶ mol) in dry solvent (50 mL) was prepared in another schlenk flask under argon atmosphere. Dry solvent (100 mL), the silylated compound solution and then the TCA solution were successively added in the silanization flask at 20 °C. The substrates were kept immersed under argon atmosphere for 12 h at 20 °C. They were washed by sonicating in the grafting solvent (2 × 5 min), water (2 × 5 min) and chloroform (2 × 5 min), respectively, and dried under nitrogen flow. Chloroform was used as the grafting solvent to prepare iSAM-Carba-Pht and iSAM-Urea-Pht. Toluene was used as the grafting solvent to prepare iSAM-Alk-Pht.

Formation of phthalimide-terminated SAMs by the spin coating technique (scSAM): Freshly prepared organosilane was dissolved in dry solvent under inert atmosphere to prepare a solution at 4.10⁻³ M. 40 μL of this freshly prepared solution was used to spin coat the substrate (rotated at 6000 rpm for 40 s). The sample was dried at ambient temperature (23 °C) in a laminar flow hood for the required time (6 h for scSAM-Urea-Pht, 8 h for scSAM-Carba-Pht, 14 h for scSAM-Alk-Pht), then washed by sonicating in the solvent used (2 × 5 min), water (2 × 5 min) and chloroform (2 × 5 min), and dried under nitrogen flow. Chloroform was used as the grafting solvent to prepare scSAM-Urea-Pht and scSAM-Carba-Pht. Both toluene and chloroform were used as the grafting solvents to prepare scSAM-Alk-Pht.



Scheme 1. A) Synthesis of phthalimide carbamate silylated (Si-Carba-Pht) coupling agent (3): a) aminohexanol, DMF, reflux, 25 h; b) allylisocyanate, Et₃N, DMF, 80 °C, 20 h; c) HSi(OMe)₃, cat. Karstedt (0.0125 eq. Pt), 60 °C, 1 h. B) Synthesis of phthalimide urea silylated (Si-Urea-Pht) coupling agent (7): d) amino compound, Et₃N, EtOH, reflux 20 h; e) TFA, CH₂Cl₂, 1 h, RT; f) allylisocyanate, DMF, Et₃N, 20 h, RT; g) HSi(OMe)₃ (5 eq.), CHCl₃, cat. Karstedt (0.0125 eq. Pt), 60 °C, 1 h. C) Synthesis of phthalimide alkyl silylated (Si-Alk-Pht) coupling agent (9): h) undecene amine, DMF, reflux, 24 h; i) HSi(OMe)₃ (5 eq.), MeCN, cat. Karstedt (0.0125 eq. Pt), 60 °C, 1 h.

2.4. Chemical surface modification

Deprotection of phthalimide groups: The phthalimide-terminated SAMs were washed by sonicating in CHCl₃ (2 × 5 min) and in water (5 min). Deprotection of the terminal phthalimide groups of SAMs was performed by immersion in a solution of MeNH₂ 40% in water for 4 min at room temperature. After, the amino-terminated SAMs were washed using an ultrasonic bath for 5 min successively with Milli-Q water, DMF/Milli-Q water (1:1, v/v), 2-propanol, CHCl₃ and dried under nitrogen flow.

Immobilization of fluorescent coumarin derivative on amino-terminated SAMs: 7-(diethylamino)coumarin-3-carboxylic acid (10.5 mg, 0.04 mmol, 1 eq) was diluted in 6 mL of dry DMF. *N*-Hydroxysuccinimide (NHS) (5.1 mg, 0.44 mmol, 1.1 eq) and 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide Hydrochloride (EDC) (8.4 mg, 0.44 mmol, 1.1 eq) were introduced and the mixture was stirred for 1 h at room temperature. Freshly prepared amino terminated SAM was deposited in a steriplan soda-lime petri dish (diameter: 60 mm; height: 15 mm), covered by the solution and 2 mL of DMF were added to fully immerse the slide. After 24 h at room temperature under inert atmosphere on an orbital shaker, the slide was washed by sonicating in DMF (2 × 5 min), Milli-Q water (2 × 5 min), EtOH (2 × 5 min) and CHCl₃ (2 × 5 min) and was dried under nitrogen flow.

2.5. Characterization of monolayers

PM-IRRAS analysis: PM-IRRAS experiments were performed on a FTIR spectrometer equipped with a PM-IRRAS optical bench,⁵⁰ following the experimental procedure previously published.⁴⁹ The

PM-IRRAS spectra were recorded at a 4 cm⁻¹ spectral resolution during 4 h acquisition time. The PM-IRRAS spectra were calibrated in order to be presented in IRRAS units (i.e. 1-Rp(d)/Rp(0), where Rp(d) and Rp(0) stand for the p-polarized reflectance of the film/substrate and bare substrate systems, respectively).⁵¹ All spectra were collected in a dry-air atmosphere, after 30 min of incubation in the chamber.

AFM measurements: AFM height images of SAMs were performed on a Bruker's Dimension Icon Atomic Force Microscope (AFM) System in PeakForce QNM® mode (Quantitative Nanomechanical Mapping) with ScanAsyst-Air tips (APEX = 2 nm, spring constant k = 0.4 N/M). The AFM height images are representative of three different areas.

Wettability measurements: Contact angles values were determined on a Krüss DSA 100 goniometer at 20 °C in static mode. The results correspond to the average of at least 3 measurements.

Fluorescence measurements: Fluorescence spectra were recorded on a Spex 1680 0.22m Double Spectrometer. The excitation source is a xenon lamp (Osram XBO 450 W, 27 A), the detector is a water refrigerated photomultiplier (Products For Research Model R928) and the integration time for measurements is 0.5 s.

3. Results and discussion

3.1. Synthesis of phthalimide-terminated silylated coupling agents

Amine group functionalization at the solid-liquid interfaces generally uses commercial organosilanes such as APTES or APTMS. However, the grafting of these organosilanes leads to complex layers due to the multiple hydrogen bond interactions between the terminal amine groups with the surface silanols and with neighboring molecules, limiting the accessibility of amino groups for subsequent chemical modification. The preparation of homogeneous amino-terminated monolayers requires using a phthalimide as a protected amino group to prevent non-covalent interactions with other polar groups at the surface.

The phthalimide coupling agent with a carbamate Si-Carba-Pht **3** was synthesized in three steps (Scheme 1A). Firstly, the alkyl part of the spacer was introduced via an addition-elimination reaction of 6-aminohexanol on phthalic anhydride. The terminal alkene group was introduced by the reaction of alcohol **1** with allylisocyanate, via carbamate bond formation. The corresponding alkene derivative **2** was obtained in good yield (76 %). The insertion of the Si(OMe)₃ group was achieved by hydrosilylation reaction of the unsaturated precursor **2** with HSi(OMe)₃ used as solvent in the presence of Karstedt's catalyst.²⁹

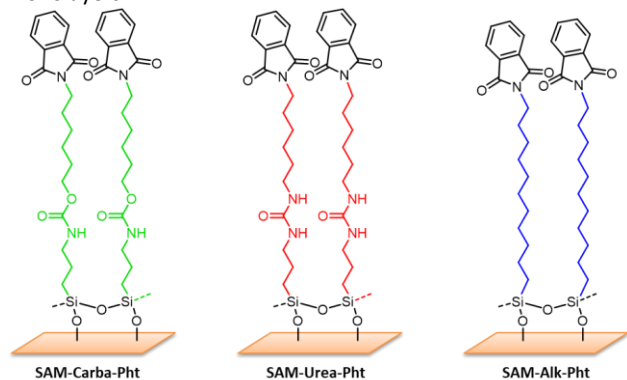
The analog ureido silylated coupling agent Si-Urea-Pht **7** was synthesized according to the previous work in four steps from phthalic anhydride (Scheme 1B).⁴² The first step consisted of introducing the alkyl chain containing the Boc-protected amine group. After the deprotection with trifluoroacetic acid (TFA), the amine compound **5** has been coupled with allylisocyanate to form the urea derivative **6** in good yield (71 %). Finally, the ureido silylated coupling agent **7** was obtained by hydrosilylation reaction of the unsaturated precursor **6** with an excess of HSi(OMe)₃ in the presence of Karstedt's catalyst.

The phthalimide alkyl silylated coupling agent Si-Alk-Pht **9** was synthesized in only two steps (Scheme 1C). Firstly, the unsaturated phthalimide precursor **8** with an alkyl chain as a spacer was synthesized in 51% yield. The addition of Si(OMe)₃ group was achieved by hydrosilylation reaction of the unsaturated precursor **8** with an excess of HSi(OMe)₃ (5 eq.) in the presence of Karstedt's catalyst.

All the alkene-terminated phthalimide compounds were hydrosilylated just before the grafting process because the corresponding trimethoxysilanes were easily hydrolyzed. Three synthesized Phthalimide-terminated silanes were immobilized by using the conventional solution immersion method (iSAM) and the spincoating process (scSAM). Phthalimide-terminated SAMs on silica substrate are schematized in Scheme 2.

3.2. Characterization of phthalimide-terminated monolayers

The PM-IRRAS spectra of phthalimide-terminated SAMs are presented in Figure 1 in the 3100-1350 cm⁻¹ spectral range for the two different methods of deposition. The functionalization of the substrate by phthalimide-terminated monolayer was confirmed by PM-IRRAS measurements which reveal the presence of the antisymmetric ($\nu_a\text{CH}_2$) and symmetric ($\nu_s\text{CH}_2$) stretching modes of the methylene groups as well as the in-plane (νCOip) and out-of-plane (νCOop) stretching mode of the carbonyl groups of phthalimide moiety. The νCOip and νCOop bands were observed close to 1770 cm⁻¹ and 1710 cm⁻¹, respectively, for all the monolayers.



Scheme 2. Schematic representation of the phthalimide-terminated SAMs.

The wavenumbers of the antisymmetric ($\nu_a\text{CH}_2$) and symmetric ($\nu_s\text{CH}_2$) stretching modes of methylene groups are sensitive to both the conformation (gauche or trans) and the order of the alkyl chains. The $\nu_a\text{CH}_2$ and $\nu_s\text{CH}_2$ bands were observed close to 2929 cm⁻¹ and 2855 cm⁻¹, respectively, for all the phthalimide-terminated monolayers, which indicate disorder alkyl chains in the monolayers with the presence of gauche conformers.

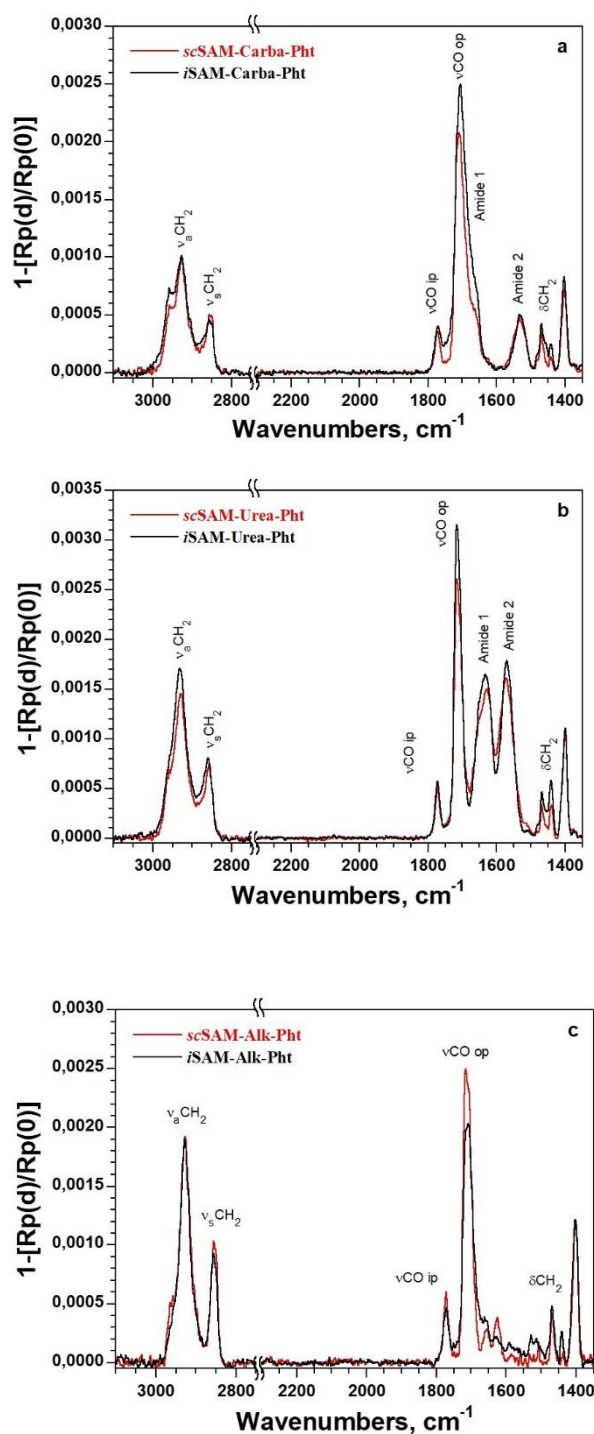


Fig. 1 PM-IRRAS spectra of the phthalimide-terminated SAMs with a) carbamate, b) urea and c) alkyl chain as spacer grafted onto SiO₂/Au substrate depending on the deposition processes in the 3100-1350 cm⁻¹ spectral range.

SAM-Urea-Pht and SAM-Carba-Pht exhibit two broad bands at 1632 (1690) cm⁻¹ and at 1571 (1532) cm⁻¹, attributed to the amide I (νC=O) and amide II (δNH+νC-N) modes of urea (carbamate) group, respectively. The presence of hydrogen bonding between the molecules is shown by the wavenumber difference (Δν) between the amide I and amide II modes. The Δν values of 61 cm⁻¹ and 158 cm⁻¹ are indicative of strong association of urea groups, and to a lesser degree of carbamate groups, by intermolecular hydrogen bonds in the phthalimide-terminated monolayers. These values are similar to the one measured for the precursors in the solid state with Δν 40 cm⁻¹ and 143 cm⁻¹ for urea and carbamate, respectively and significantly lower than those observed in diluted solution (Δν = 132 cm⁻¹ and 195 cm⁻¹ for urea and carbamate, respectively) in absence of hydrogen bonding.⁴⁶ Due to the disordered nature of the alkyl chains, the self-assembly of the monolayer depends mainly on the establishment of intermolecular hydrogen bonds between the carbamate or urea groups in the monolayers.

The presence of urea and carbamate groups embedded in the alkyl chains is not favorable to form well-ordered SAMs because the distance between alkyl chains is too large to establish van der Waals interactions. However, the alkyl chains of SAM-Alk-Pht are also disordered, suggesting that the large size of phthalimide end group influences the organization of the monolayers. In addition, the intensities measured on the PM-IRRAS spectra for the methylene bands are similar for SAM-Urea-Pht and SAM-Alk-Pht showing the same packing density of the monolayers limited by the size of the phthalimide unit. For SAM-Carba-Pht these intensities are weaker suggesting less densely packed monolayer. The use of the carbamate group is less efficient for the self-assembly of the molecules in the monolayer than the urea group. Indeed, the self-assembly of monolayer by intermolecular hydrogen bonding is less strong for the carbamate group because it can establish only two hydrogen bonds against four for the urea group. These results show clearly the influence of the molecular structure on the packing density.

The phthalimide-terminated SAMs were also characterized by atomic force microscopy (AFM). The AFM height images reveal that the monolayers are homogenous and similar regardless of the deposition methods (see supporting information). The root-mean-square (rms) roughnesses were around 1.2 nm which is close to the uncovered substrate (0.9 nm).

The nature of the spacer and the roughness of the monolayer influence the water contact angle measurements, SAM-Carba-Pht and SAM-Urea-Pht showed similar values with 52°±1 and 50°±1, respectively, while the value was higher 58°±1 for SAM-Alk-Pht. The latter value is consistent with previously reported study for phthalimide-terminated alkyl monolayer prepared by a post-functionalization method from the corresponding bromo-terminated SAM.³⁶ So, the direct grafting of silylated phthalimide alkyl compounds gives a monolayer similar to the one obtained by the post-functionalization method. The presence of a polar group (carbamate or urea) in the alkyl chain can explain lower contact angle values for SAM-Carba-Pht and SAM-Urea-Pht. The values for each type of SAMs are similar whatever the deposition methods.

The preparation of well define amino-terminated monolayers by a direct grafting strategy requires the use of phthalimide as a protected amino group to prevent non-covalent interactions with polar groups at the surface. The qualities of the three types of monolayers are similar regardless of the deposition method used (immersion or spin coating). These results highlight the possibility to prepare phthalimide-terminated monolayers by using the spin coating process, which is fast and uses very small amounts of solvent for the deposition step. In addition, the use of phthalimide as a protected amino group has demonstrated its efficiency to obtain a well-defined monolayer in one step by both deposition methods.

3.3. Characterization of amino-terminated monolayers

The conversion of the phthalimide protecting group into the amino groups was achieved using an aqueous solution of methylamine in four minutes. The PM-IRRAS spectra of phthalimide-terminated and amino-terminated scSAMs are compared in Figure 2. The successful reaction was confirmed for all types of phthalimide-terminated SAMs by the total disappearance of the two characteristic bands close to 1770 cm⁻¹ (νCOip) and 1710 cm⁻¹ (νCOop) of the phthalimide moiety. For scSAM-Alk-NH₂ a new broad band appeared clearly at around 1645 cm⁻¹, assigned to the bending mode (δNH₂) of the amino end groups. For scSAM-Carba-NH₂ and scSAM-Urea-NH₂, the characteristic band of amino groups overlapped with the amide I band of carbamate and urea groups in the same region. The positions of amide I and amide II bands remain unchanged, indicating that the self-assembly by intermolecular hydrogen bonds is similar after the deprotection reaction. The intensity of amide II is also similar before and after the conversion in SAM-NH₂, revealing the good stability of the monolayers. In addition, the wavenumbers of methylene stretching bands observed at 2929 cm⁻¹ (νaCH₂) and 2855 cm⁻¹ (νsCH₂) are similar for SAM- phthalimide and SAM-NH₂, revealing that the organization of the grafted molecules onto substrate were not modified. This behaviour is consistent with the previous study showing that the shorter alkyl chains less than 16 carbon atom possess a high degree of conformational disorder.⁵²

The increase of the surface's hydrophilicity of the SAM-NH₂ was confirmed by contact angle measurements for the monolayers prepared by both spin coating and immersion methods. After the deprotection reaction, the contact angles decreased significantly to 44°±1, 40°±1 and 48°±1, for scSAM-Carba-NH₂, scSAM-Urea-NH₂ and scSAM-Alk-NH₂ respectively. These values are similar to that measured for the commercially available amino-propyl triethoxysilane based layer (43°), but lower than those measured for long amino alkyl SAMs (60° for C11-NH₂ and 78° for C21-NH₂) for which a disordered structure with more exposure of the alkyl chains can explain this result.^{34,36,53}

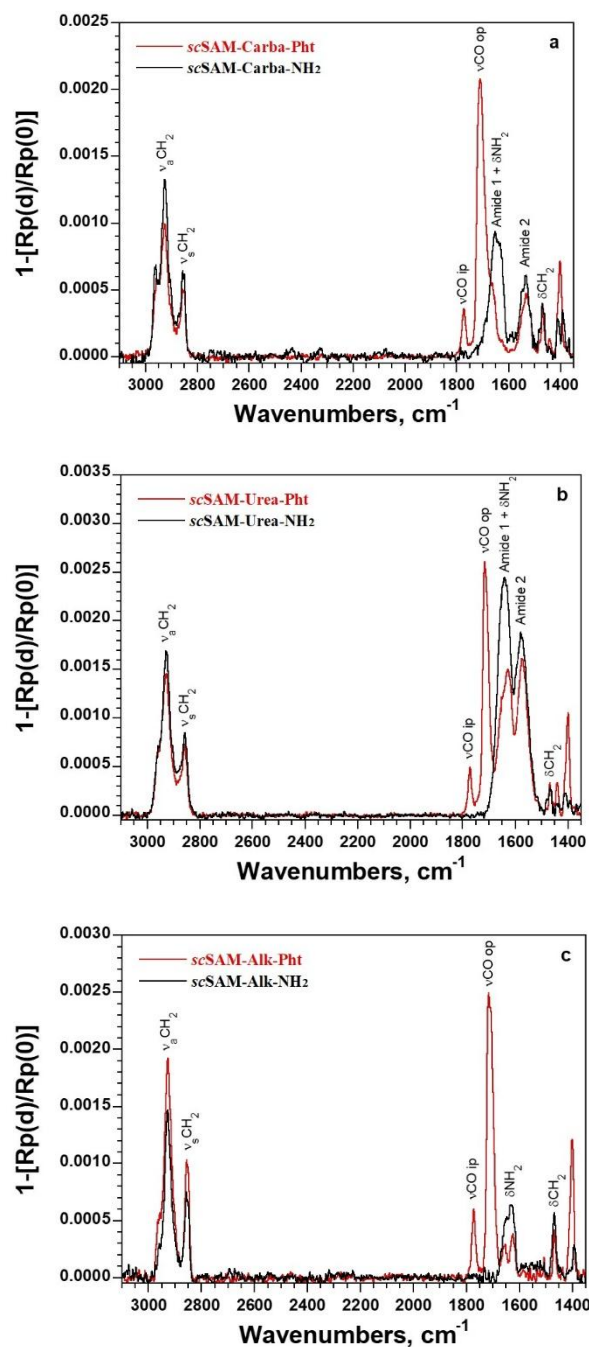


Fig. 2 PM-IRRAS spectra in the 3100-1350 cm^{-1} spectral range of the phthalimide-terminated SAMs prepared by spin coating and converted in amino-terminated SAMs with a) carbamate, b) urea and c) alkyl chain as spacer.

The reactivity of SAMs-NH₂ was studied using a coumarin derivative as a fluorescent probe. The peptide-like coupling of coumarin derivative bearing a carboxylic function with the amino end group on SAMs required the activation step by using the carbodiimide

chemistry to afford the corresponding succinimide ester (Figure 3a). After chemical modification, the monolayers were analyzed by fluorescence and PM-IRRAS spectroscopies.

The reactivity of SAM-NH₂ towards peptide-like coupling was confirmed in Figure 3 by PM-IRRAS with the presence of several bands related to the coumarin moiety ($\nu\text{C}=\text{O}$ at 1710 cm^{-1}) and to the amide link (amide I at 1625 cm^{-1} and amide II at 1550 cm^{-1}).

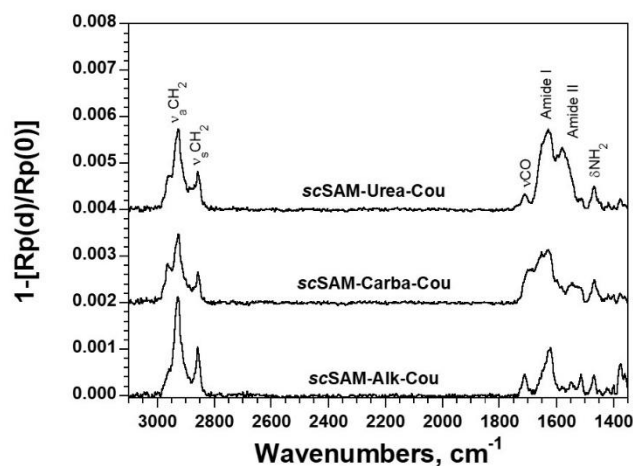


Fig. 3 PM-IRRAS spectra of scSAM-Alk-Cou, scSAM-Carba-Cou and scSAM-Urea-Cou.

Figure 4b shows the fluorescence spectra of scSAM-Alk-Cou, scSAM-Carba-Cou and scSAM-Urea-Cou with maximal emission peaks at 476 nm, 468 nm and 462 nm, respectively. These fluorescence emission peaks are characteristic of the coumarin moiety, showing the successful grafting of the fluorophores on all scSAM-NH₂.⁵⁴

The fluorescence properties of coumarin derivative in solution ($\lambda_{\text{em}} = 466 \text{ nm}$ /DMF) and film ($\lambda_{\text{em}} = 530 \text{ nm}$) are very different (Figure 4c). In solution at low concentration, the fluorophores are sufficiently separated showing the fluorescence spectrum of isolated chromophore. For the solid film, the concentration of fluorophores groups is higher at the surface, leading to a redshift (88 nm) of emission band of coumarin moieties due to a new excimer emission.⁵⁵ For scSAM-Alk-Cou, the peak is larger due to the presence of a shoulder at 505 nm, related to the excimer species coming from the closer proximity of the coumarin groups in this monolayer. This shoulder reveals a high amount of chromophore onto the surface, consistent with the higher packing density of amine groups. This behavior is similar to the fluorescence property observed for the coumarin solid film.

scSAM-Carba-Cou and scSAM-Urea-Cou have a lower amount of chromophore because this shoulder is less important, leading to smaller peak widths and the fluorescence spectra become closer than that observed for coumarin in diluted solution.

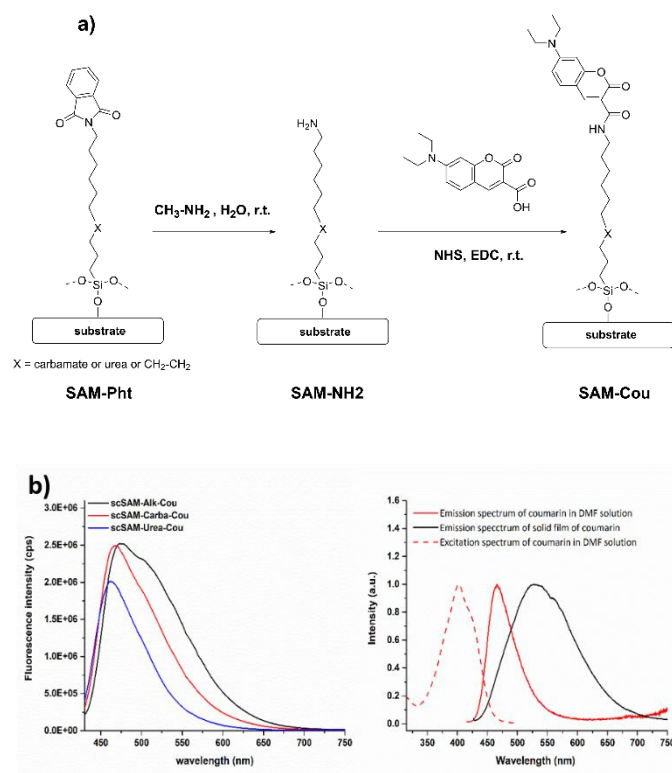


Fig. 4 a) Coupling reaction of the coumarin derivative onto SAM-NH₂; b) Fluorescence spectra of scSAM-Cou c) Excitation spectrum and fluorescence spectra of coumarin derivative in solution and in solid state.

The higher fluorescence intensities for scSAM-Carba-Cou suggest that amine groups are more accessible to react with coumarin. For scSAM-Urea-Cou the packing density of the amine groups is higher than the scSAM-Carba-Cou, which could induce steric hindrance, and render less accessible the amine groups. In the case of scSAM-Alk-Cou, the flexibility of long alkyl chain (11 carbon atoms) can contribute to the good reactivity of the amine groups compared to the smaller alkyl chain (6 carbon atoms) of scSAM-Carba-Cou and scSAM-Urea-Cou. These results shown that the packing density of the terminal amino group have an impact on the post-grafting treatment. The same behavior has been observed for the corresponding SAMs prepared by the immersion solution method (see supporting information). Finally, the accessibility of the exposed amino groups depends mainly on the molecular structure which are responsible of the self-assembly of the monolayers.

4. Conclusion

The functionalization of surfaces with amine groups using commercial silanes is very sensitive to the experimental conditions and the molecular organization. The multiple interactions possibilities of the free amino end group promote disordered aminosilane layers. This can affect the stability and the accessibility of the reactive groups as well as the effectiveness of further grafting of molecules onto the surface. In this article, well defined amino-terminated monolayers were obtained by a direct grafting strategy using phthalimide as a protected amino group to prevent

non-covalent interactions with polar groups at the surface. We performed successfully the grafting of phthalimide-terminated SAMs by using both the classic immersion method and the spin coating process. The total conversion of the phthalimide protecting groups into the amino groups was demonstrated without any degradation for all phthalimide-terminated SAMs. Whatever the nature of the spacer (pure alkyl, urea, or carbamate) the size of the terminal phthalimide group induces a disorder of the alkyl chains, which persists after deprotection. Finally, the reactivity of the exposed amino groups depends on the packing density of the monolayers and the flexibility of the alkyl segment in the molecular structure. These results highlight the possibility to prepare phthalimide-terminated monolayers by using the spin coating process, which is fast and eco-friendly for the deposition step.

Author Contributions

Lisa Rouvière: Investigation. Axelle Hachin: Investigation. Christian Aupetit: Investigation, Formal analysis, Visualization. Julien Hunel: Visualization, Investigation. Svitlana Shinkaruk: Conceptualization. Thierry Buffeteau: Validation, Investigation, Writing - original draft, Writing - review & editing, Visualization. Emilie Genin: Supervision, Conceptualization, Writing - review & editing. Luc Vellutini: Supervision, Conceptualization, Writing - original draft, Writing - review & editing.

Conflicts of interest

There are no conflicts to declare

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