



HAL
open science

Silane-based SAMs deposited by spin coating as a versatile alternative process to solution immersion

Lisa Rouvière, Nisreen Al-Hajj, Julien Hunel, Christian Aupetit, Thierry Buffeteau, Luc Vellutini, Emilie Genin

► **To cite this version:**

Lisa Rouvière, Nisreen Al-Hajj, Julien Hunel, Christian Aupetit, Thierry Buffeteau, et al.. Silane-based SAMs deposited by spin coating as a versatile alternative process to solution immersion. *Langmuir*, 2022, 38 (20), pp.6464-6471. 10.1021/acs.langmuir.2c00668 . hal-03839846

HAL Id: hal-03839846

<https://hal.science/hal-03839846v1>

Submitted on 4 Nov 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Silane-based SAMs deposited by spin coating as a versatile alternative process to solution immersion

Lisa Rouvière,^a Nisreen Al-Hajj,^{a,b} Julien Hunel,^a Christian Aupetit,^a Thierry Buffeteau,^a Luc Vellutini^{a*} and Emilie Genin^{a*}

^a Univ. Bordeaux, CNRS, Bordeaux INP, ISM, UMR 5255, F-33400 Talence, France

^b Department of Chemistry, Faculty of Science, An-Najah National University, P.O. Box 7, Nablus, Palestine

Corresponding Authors

*E-mail: luc.vellutini@u-bordeaux.fr and emilie.genin@u-bordeaux.fr

ABSTRACT

Functionalization of silica surfaces with silane-based self-assembled monolayers (SAMs) is widely used in material sciences to tune surface properties and introduce terminal functional groups enabling subsequent chemical surface reactions and immobilization of (bio)molecules. Here, we report on the synthesis of four organotrimethoxysilanes with various molecular structures and we compare their grafting by spin coating with the one performed by the conventional solution immersion method. Strikingly, this study clearly demonstrates that the spin coating technique is a versatile, fast and more convenient alternative process to prepare robust, smooth and homogeneous SAMs with similar properties and quality as those deposited via immersion. SAMs were characterized by PM-IRRAS, AFM, and wettability measurements. SAMs can undergo several chemical surface modifications and the reactivity of amine-terminated SAM was confirmed by PM-IRRAS and fluorescence measurements.

INTRODUCTION

The functionalization of surfaces remains a key challenge in material sciences to control surface properties (wettability, adhesion, biocompatibility, antifouling, etc) and to introduce desired exposed reactive organic functions for subsequent chemical surface reactions and immobilization of (bio)molecules. It is necessary for a variety of applications in the fields of molecular electronics,¹ microfluidics,² optics,³ catalysis,⁴ biotechnology⁵⁻⁸ and biosensors.^{9,10} Covalent chemical modification is usually preferred to physical adsorption because it is more robust thanks to its irreversible bonding. A widely used strategy for functionalizing silica substrates is the grafting of organic self-assembled monolayers (SAMs) enabling covalent chemical modification with a molecular level control.¹¹⁻¹³ The formation of SAMs onto silica substrates^{11,12} have been successfully achieved using molecules with anchoring groups such as silanes,¹³⁻¹⁵ phosphonic acids¹⁶⁻¹⁸ and more recently alcohols.¹⁹ The most common approach involves the reaction of silylated coupling agents as the corresponding SAMs are often more stable and homogeneous with uniform surface coverage. Indeed, the grafting process of such molecules involves a

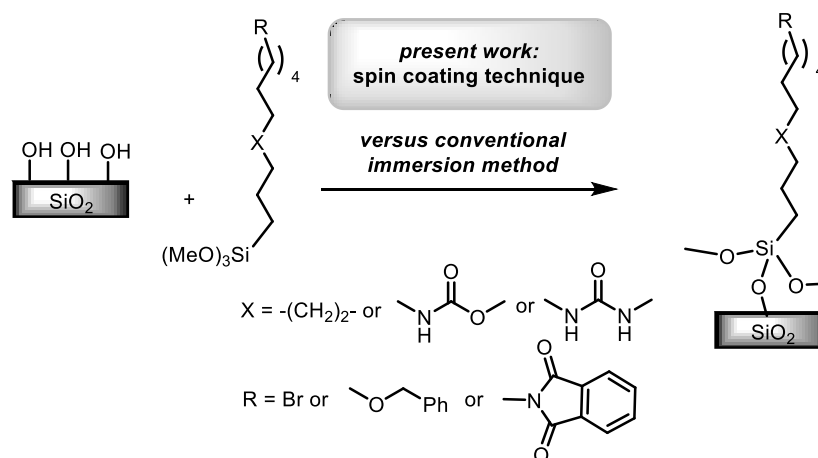
covalent anchoring with the silanol groups onto the surface as well as a partial in plane polymerization of the molecules through siloxane (Si-O-Si) bonds for silanes bearing more than one hydrolysable group. Trichloro- and trialkoxyorganosilanes are among the mostly used organosilylated compounds. Trimethoxysilylated coupling agents appeared to be a good compromise in terms of reactivity, ease of handling and quality of the obtained SAMs (smoothness and homogeneity) as they are less prone to the formation of aggregates than trichlorosilanes.²⁰

Since silane-based SAMs onto silica substrates have so many applications, a lot of research efforts have been dedicated for decades to develop techniques for their fabrication.^{1,11} For surface modification with silanes two deposition methods are commonly used: reactions in solution or in the vapor phase. The conventional solution immersion method consists in immersing clean substrates in an incubator containing a diluted solution of silylated coupling agent, for a specified time and under controlled conditions (inert atmosphere, control of the amount of water, control of the temperature, etc).²⁰⁻²² One of the main drawbacks is that it requires quite a lot of organic solvent and thus produce significant unfriendly chemical wastes. In contrast, the chemical vapor deposition (CVD) method consists in the exposure of a clean substrate to silane vapor, which do not require organic solvents.²³⁻²⁶ However, CVD has to be performed in a sealed container in ultra-high vacuum conditions and generally at elevated temperature (150°C-200°C) which may not be compatible with some sensitive organic functions, although deposition at room temperature may be possible in some cases. Other processes have been more rarely applied for the preparation of silane-based SAMs and less extensively studied in details such as the Langmuir-Blodgett^{27,28} method and the spin coating technique.²⁹

Among these two, the spin coating technique, commonly used for thin films or multilayers deposition on planar substrates, attracts particular attention as an alternative to conventional SAMs deposition methods. Indeed, it has the advantages of being fast, simple, easy to handle, conducted in ambient conditions and less demanding in terms of organic solvent. Monolayers derived from SiCl₃-terminated carbosilane dendrons,³⁰ *p*-tolyltrichlorosilane³¹ and octadecylsilanes^{29,32} have been afforded using the spin coating technique. More recently, we reported the first functional SAM elaborated via this technique. Indeed, we demonstrated the successful preparation of the azide-terminated SAM by spin coating a solution of an azidoorganosilane onto a silica substrate.³³ The reactivity and the robustness of this SAM towards copper catalyzed alkyne-azide cycloaddition (CuAAC) were demonstrated by reacting a probe molecule bearing a NO₂ group and performing Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS) measurements. Moreover, we also evidenced that azide-terminated SAM display a singular behavior due to the dipolar character of the N₃ group. Indeed, the orientation of azido dipoles at the surface depends strongly on the method used to prepare the azide-terminated SAM and it strongly influences the accessibility and reactivity of the azides.³⁴

The aim of this work is to evaluate the scope of the spin coating technique for the preparation of silane-based SAMs and demonstrate that it can be a general, versatile and convenient alternative process in comparison with the conventional solution immersion method (Scheme 1). In this paper, we report on the synthesis of four organotrimethoxysilanes with various molecular architectures and their grafting onto silica substrates by both spin coating and solution immersion

methods in order to compare. We focused on compounds terminated by a bromide, a benzyl or a phthalimide group and featuring either a pure alkyl spacer or an alkyl chain incorporating an internal carbamate or urea function. We also investigated the robustness and the reactivity of the spin coated SAMs by performing subsequent chemical surface modifications to provide azide- or amine-terminated SAMs and finally use the latter one to immobilize a fluorescent molecule by peptide coupling. Chemical modifications of the surfaces have been investigated systematically using PM-IRRAS, Atomic Force Microscopy (AFM), wettability measurements and also fluorescence spectroscopy, when relevant.



Scheme 1 Schematic representation for the preparation of trimethoxyorganosilane-based SAMs onto silica substrates and structures of the coupling agents used in this work

EXPERIMENTAL SECTION

Synthesis of the intermediate compounds and of the coupling agents

The syntheses and characterizations of the organic compounds are reported in details in the ESI.

Silanization protocols

Substrate preparation

The SiO_2/Au substrates were supplied by Optics Balzers AG. They correspond to Goldflex mirror with SiO_2 protection layer (GoldflexPRO, reference 200785). Their absolute reflectance was higher than 98% in the 1.2–12 μm spectral range. The thickness of the SiO_2 layer, measured by ellipsometry, was $215 \pm 7 \text{ \AA}$, using a refractive index of 1.46 (Ielli2000 NFT ellipsometer, $\lambda = 532 \text{ nm}$). A homogeneous surface was observed by atomic force microscopy (AFM) with a root mean square (rms) roughness of 9 \AA (Thermomicroscope Autoprobe CP Research, Park Scientific). Before each surface functionalization, the SiO_2/Au substrates were washed with Milli-Q water (18 $\text{M}\Omega\cdot\text{cm}$), sonicated in chloroform for 15 min, activated by UV-ozone (185–254 nm) for 30 min. They were immediately used for silanization by spin coating. For the conventional solution immersion method, they were introduced immediately into the silanization flask, let under reduced pressure for 1 h 30 and then stored under argon atmosphere.

Silanization by the immersion method

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} M) 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 (for hydrogen-bonding SAMs) and 16h (for SAM-Br) at 20 °C. They were washed by sonicating in the grafting's 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 **im-SAM-Br** and **im-SAM-7**. Toluene was used as the grafting solvent to prepare **im-SAM-3** and **im-SAM-10**.

Silanization by the spin coating technique

Freshly prepared organosilane was dissolved in dry solvent under inert atmosphere to prepare a solution at 4×10^{-3} M. 40 μ L of this freshly prepared solution of organosilane 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 (3h for **sc-SAM-Br** and **sc-SAM-7**, 13h for **sc-SAM-3**, 14h for **sc-SAM-10**), then washed by sonicating in the solvent used (2×5 min), water (2×5 min) and chloroform (2×5 min), respectively, and dried under nitrogen flow. In addition, the washing process was optimized to remove excess material. The dynamic washes were tested and did not achieve the monolayer.

Chloroform was used as the grafting solvent to prepare **sc-SAM-Br** and **sc-SAM-7**. Toluene was used as the grafting solvent to prepare **sc-SAM-3** and **sc-SAM-10**.

Protocols for surface chemical modifications

Nucleophilic substitution of bromide with azide

The bromine terminated monolayers were immersed in a saturated solution of sodium azide in dry DMF for 48 h at room temperature under argon atmosphere. The substrates were subsequently sonicated for several minutes in DMF, water and chloroform, respectively, and dried under nitrogen flow.

Deprotection of phthalimide

The phthalimide terminated monolayer was washed by sonicating in CHCl_3 (2×5 min) and in water (5 min). The slide was then introduced into a solution of MeNH_2 40% in water. After 4 min, the slide was washed by sonicating in water (5 min), DMF/ H_2O 1:1 (5 min), $i\text{PrOH}$ (5 min) and CHCl_3 (5 min) and dried under nitrogen flow.

Immobilization of 7-(diethylamino)coumarin-3-carboxylic acid on SAM-NH₂

7-(diethylamino)coumarin-3-carboxylic acid (10.5 mg, 0.04 mmol, 1 eq) was diluted in 6 mL of dry DMF. NHS (5.1 mg, 0.44 mmol, 1.1 eq) and EDC (8.4 mg, 0.44 mmol, 1.1 eq) were introduced. The mixture was stirred for 1h 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 24h at room temperature under inert atmosphere on an orbital shaker, the slide was washed by sonicating in DMF (2×5 min), water (2×5 min), EtOH (2×5 min) and CHCl_3 (2×5 min) and were dried under nitrogen flow.

Characterizations of SAMs

AFM measurements.

AFM height images of SAMs on SiO₂/Au substrates 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.

PM-IRRAS experiments.

PM-IRRAS experiments were performed on a ThermoNicolet Nexus 670 FTIR spectrometer equipped with a PMIRRAS optical bench, following the experimental procedure previously published.^{35,36} The PM-IRRAS spectra were recorded at a resolution of 4 cm⁻¹ during 4 h acquisition time. The PM-IRRAS spectra were calibrated in order to be presented in IRRAS units.^{36,37} All spectra were collected in a dry-air atmosphere after 30 min of incubation in the chamber. All spectra in the figures are average of at least 4 spectra.

Wettability measurements.

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

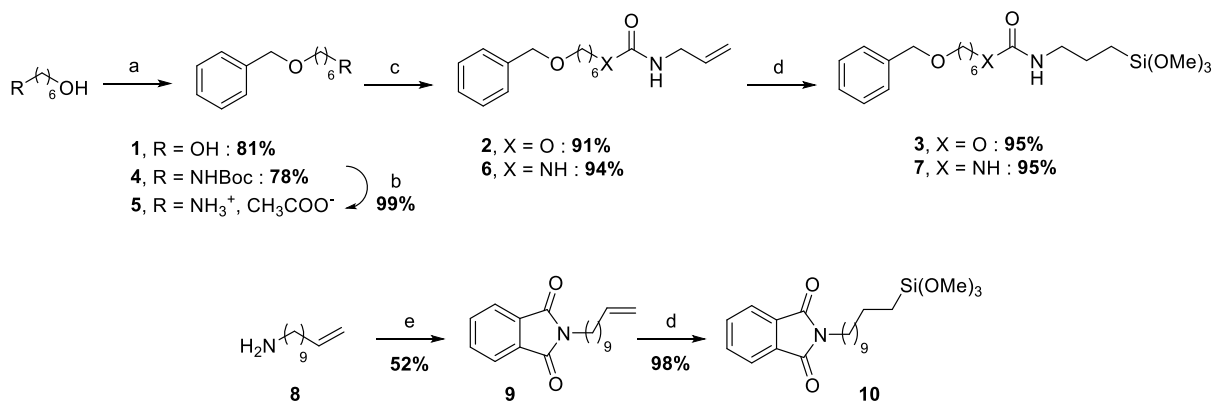
Fluorescence measurements.

Fluorescence spectra were recorded on a Spex 1680 0.22m Double Spectrometer.

RESULTS AND DISCUSSION

Synthesis of the silylated coupling agents

To elaborate the SAMs, four silylated coupling agents displaying various molecular structures were considered. The 11-bromoundecyltrimethoxysilane was freshly prepared following our previously reported procedure.³⁴ For this purpose, we also synthesized three original organotrimethoxysilanes with a pure alkyl chain or one containing either a carbamate or a urea group and possessing either a benzyl- or a phthalimide-terminal group (Scheme 2).



(a) BnBr, NaH, THF or DMF, r.t., 3d; (b) TFA, CH₂Cl₂, r.t., 1h or 48h; (c) allylisocyanate, Et₃N, THF or DMF, r.t or reflux, 20h to 36h; (d) HSi(OMe)₃, Karstedt's catalyst, 1h to 3h, r.t. or 60°C, neat or CH₃CN or CHCl₃; (e) phthalic anhydride, DMF reflux, 24h.

Scheme 2 Synthesis of silylated coupling agents

The benzyl-terminated coupling agent with an internal carbamate group **3** was achieved in three steps from commercially available reagents. First, desymetrization of the 1,6-hexanediol by monoalkylation with benzylbromide in the presence of sodium hydride led to the compound **1** in high yield (81%). Then, the alcohol **1** was reacted with the allylisocyanate to afford efficiently the olefinic precursor **2**. The last step consists in its hydrosilylation reaction in the presence of Karstedt's catalyst using trimethoxysilane as solvent, yielding compound **3**.

The benzyl-terminated coupling agent with an internal urea moiety **7** was achieved in four steps following a similar synthetic route and starting from 6-(Boc-amino)-1-hexanol. Alkylation of the hydroxyl group with benzylbromide in the presence of sodium hydride provided the ether **5** in high yield (78%). After the quantitative Boc deprotection using trifluoroacetic acid, the obtained compound **5** was efficiently condensed with the allylisocyanate in the presence of triethylamine to provide the olefinic precursor **6**. Finally, the corresponding organotrimethoxysilane **7** was obtained by hydrosilylation reaction of the compound **6** in chloroform with an excess of HSi(OMe)_3 and in the presence of Karstedt's catalyst.

A two-steps synthetic route was implemented to provide the phthalimide-terminated coupling agent with an alkyl spacer **10**. 10-undecen-1-amine **8** was reacted with phthalic anhydride to give the intermediate **9**, which was hydrosilylated in acetonitrile with an excess of HSi(OMe)_3 and in the presence of Karstedt's catalyst to afford the desired trimethoxysilylated derivative **10**.

Silanization of silica substrates and characterization of SAMs

The four silylated coupling agents were used to prepare monolayers immobilized onto SiO_2/Au substrates by using two different methods of deposition. Following our previously reported protocol, a solution of compound was deposited onto clean oxide surfaces in ambient atmosphere using the spin coating technique and the modified substrates were then washed after drying to remove the excess of organosilane.^{33,34} The conventional solution immersion method was also applied to compare SAMs properties provided by the two processes.³⁴

Azide-terminated SAMs

Pursuing our recent research efforts in investigating the elaboration of azide-terminated monolayers,^{33,34} we first studied the grafting by spin coating of 11-bromoundecyltrimethoxysilane using chloroform as solvent to subsequently provide SAM- N_3 by the widely used post-chemical modification. The functionalization of the substrate by an alkylbromide monolayer via spin coating was confirmed by the PM-IRRAS analysis of **sc-SAM-Br** (Figure 1a) which shows the presence of the asymmetric ($\nu_a\text{CH}_2$) and symmetric ($\nu_s\text{CH}_2$) stretching modes of the methylene groups at 2929 cm^{-1} and 2854 cm^{-1} , respectively. These values are similar to those described previously for bromine-terminated SAM prepared by the immersion method (**im-SAM-Br**) and reveal a disorder of the alkyl chains.³⁴ The intensities measured on the PM-IRRAS spectrum of **sc-SAM-Br** for the $\nu_a\text{CH}_2$ and $\nu_s\text{CH}_2$ bands (i.e. 0.0016 and 0.0008, respectively) are also the same as those observed for the analog **im-SAM-Br**

prepared by the conventional immersion process.³⁴ It thus confirms that using the spin coating technique leads to the formation of a single monolayer onto the silica surface while allowing reducing the duration for the SAM-Br preparation from 16h to 3h. The nucleophilic substitution of bromine with azide was performed following the classical protocol involving the immersion of the substrates in a saturated solution of sodium azide in DMF. The success of the chemical modification of the surface was confirmed by the appearance of the new characteristic band of the azide group at 2100 cm^{-1} assigned to asymmetric stretching ($\nu_a\text{N}_3$) mode on the PM-IRRAS spectrum of **sc-SAM-N₃** (Figure 1a). The position and the intensity of $\nu_a\text{N}_3$ band are in agreement with the one previously reported for **im-SAM-N₃** using the conventional process (Figure 1b).³⁴ In addition, no degradation of the monolayer occurred since the methylene bands remained comparable in position and in intensity. It highlights the fact that the covalent grafting by spin coating technique is as robust as the one originating from the solution immersion process. The AFM height image evidenced a smooth and homogeneous organic monolayer without the presence of defaults (Figure S1, Supporting Information), confirming a uniform functionalization on the whole surface. The rms (root mean square) roughness of **sc-SAM-N₃** is equal to 1.29 nm which is similar to the one previously reported using the conventional process (i.e. 1.19 nm) and close to the one measured for the initial substrate (0.9 nm). Wettability measurements have also been performed to characterize **sc-SAM-N₃**. The experimental contact angle value of $66^\circ \pm 1^\circ$ is similar of **im-SAM-N₃** ($65^\circ \pm 1^\circ$) and in agreement with the one found in the literature.^{33,38} All these characterizations prove that spin coating is an efficient alternative silanization method to elaborate SAM-N₃ by post-functionalization, displaying the same properties as those provided with the conventional immersion process. The possibility to further immobilize various molecules on SAM-N₃ by click chemistry³⁴ makes them particularly popular for numerous applications.

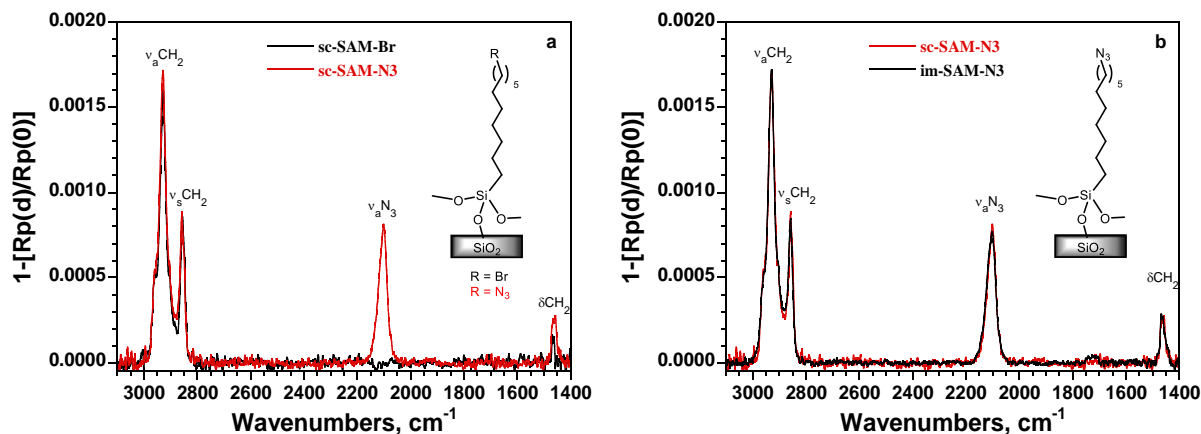


Figure 1 PM-IRRAS spectra of a) **sc-SAM-Br** prepared by spin coating and its subsequent post-functionalization to provide **sc-SAM-N₃**; b) **sc-SAM-N₃** compared to **im-SAM-N₃** obtained using the conventional immersion method from the corresponding bromine-terminated SAM.

Hydrogen-bonding benzyl-terminated SAMs

Then, we investigated the use of the spin coating technique to provide hydrogen-bonding SAMs. The grafting by spin coating of benzyl-terminated coupling agents containing internal carbamate

or urea groups (compounds **3** and **7**, respectively) onto a silica substrate was thus studied to prepare **sc-SAM-3** and **sc-SAM-7**, respectively (Figures 2a and 2b). As a comparison, the same organosilanes were also deposited using the conventional solution immersion to afford **im-SAM-3** and **im-SAM-7**, respectively. While chloroform was suitable for compound **7**, toluene appeared to be a better choice for compound **3** to get reproducible results. All SAMs were characterized by PM-IRRAS measurements. All characteristic bands corresponding to the different functional groups of the coupling agents are visible which confirm that the molecules are grafted onto the surface. **im-SAM-3**, **sc-SAM-3**, **im-SAM-7** and **sc-SAM-7** display the same wavenumbers of the $\nu_a\text{CH}_2$ and $\nu_s\text{CH}_2$ bands close to 2930 cm^{-1} and 2856 cm^{-1} , respectively, which indicate disordered alkyl chains. It is consistent with previous reports showing that the presence of internal groups prone to hydrogen-bonding (urea, amides) is not favorable to form well-ordered alkyl chains because the distance between the alkyl chains is too large.^{36,39} For monolayers incorporating carbamate or urea groups, the characteristic amide I and amide II modes were observed at 1690 (1630) cm^{-1} and 1530 (1572) cm^{-1} respectively for SAM-3 and SAM-7 independent of the deposition method. The lower $\Delta\nu$ value (difference between the wave numbers of amide I and amide II modes) for SAM-7 (58 cm^{-1}) compared to SAM-3 (160 cm^{-1}) indicates a stronger association through hydrogen bonds.⁴⁰ The intensities of the methylene bands for **sc-SAM-3** and **im-SAM-3** in comparison with **sc-SAM-7** and **im-SAM-7** are similar which evidences that these SAMs incorporated the same quantity of organic matter since the two coupling agents display the same number of CH_2 and end O-benzyl group. The analogous urea or carbamate monolayers led to similar self-assemblies.

AFM height images show smooth and homogeneous monolayers with rms roughnesses close to the value of the initial substrate (Figure S2, Supporting Information). All these SAMs display also similar wettability properties with experimental contact angle values close to 62° ($60^\circ \pm 3^\circ$, $65^\circ \pm 2^\circ$, $60^\circ \pm 2^\circ$, $62^\circ \pm 2^\circ$ for **sc-SAM-3**, **im-SAM-3**, **sc-SAM-7**, **im-SAM-7** respectively). The same immersion time (12h) in the silanization solution is needed to get a complete monolayer for **im-SAM-3** and **im-SAM-7**. Based on the intensities of the methylene bands, a saturation of the surface was observed after 12h for both coupling agents and no multilayers or aggregates were formed by extending the duration of the grafting. The deposition of compound **3** using the spin coating technique provided **sc-SAM-3** with the same properties compared to **im-SAM-3**. Although the elaboration of **sc-SAM-3** requires 13h, the spin coating technique remains advantageous as it needs less solvent and is easier to handle. In addition, **sc-SAM-7** and **im-SAM-7** display also the same properties despite the lower (higher) intensity of the amide I (amide II) band for **sc-SAM-7** which reveals an orientation of the internal C=O groups slightly more parallel to the surface due to the surface selection rule of the PM-IRRAS spectroscopy for metallic substrate. In this case, the spin coating is particularly advantageous since the duration of **sc-SAM-7** elaboration (3h) is 4-times shorter.

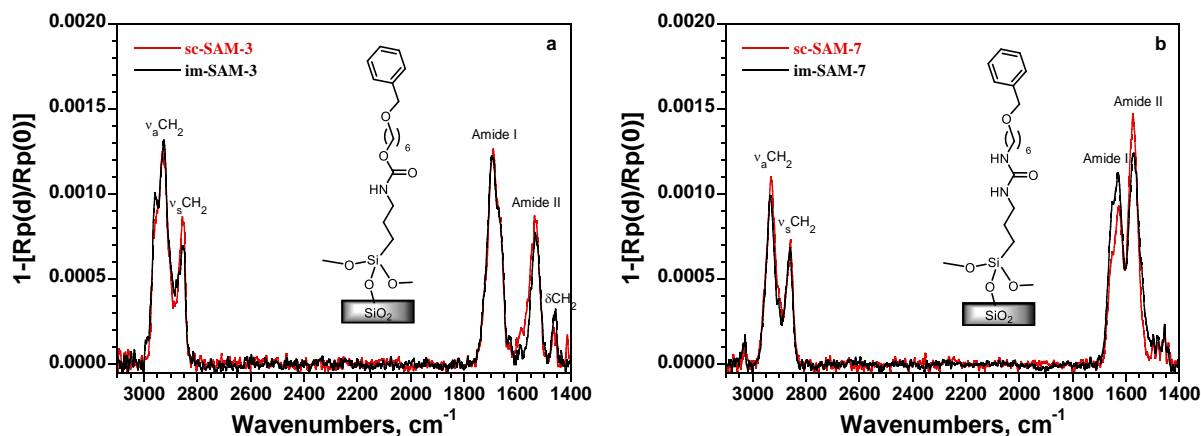


Figure 2 PM-IRRAS spectra of a) compound **3** and b) compound **7** grafted onto the SiO₂/Au substrate by spin coating (sc) and by the solution immersion method (im).

Phthalimide-terminated alkyl SAMs

Finally, we studied the grafting of the phthalimide-terminated coupling agent with an alkyl spacer **10** using toluene as solvent. Interestingly, phthalimide-terminated SAM can lead to amine-terminated SAM, widely used for various applications including biotechnological ones.⁴¹ **sc-SAM-10** was prepared via the spin coating technique and compared to **im-SAM-10** elaborated by the solution immersion method. The success of the graftings was confirmed by the observation of all the characteristic IR bands of compound **10** on the PM-IRRAS spectra (Figure 3). The bands at 1772 cm⁻¹ and 1710 cm⁻¹, assigned respectively to the in-phase and out-of-phase carbonyl stretching vibrations of the phthalimide moiety, attest the presence of the terminal group. Once again, alkyl chains are quite disordered as revealed by the position of the asymmetric and symmetric stretching vibrations (at 2929 cm⁻¹ and 2855 cm⁻¹) of the methylene groups which is in agreement with our previous reports.⁴¹ The orientation of the molecules within **im-SAM-10** and **sc-SAM-10** is the same based on the intensities and positions of the IR bands. AFM height images reveal that the monolayers were smooth and homogenous (Figure S3, Supporting Information). Indeed, rms roughnesses of around 1.2 nm and 1.3 nm were measured for **im-SAM-10** and **sc-SAM-10**, respectively, which is close to the one of the initial SiO₂/Au substrate (0.9 nm). These SAMs display also the same wettability properties with experimental contact angle values of 58° ± 2°. Thus, the spin coating technique allows the elaboration of phthalimide-terminated SAMs in a more convenient way in comparison with the conventional immersion method.

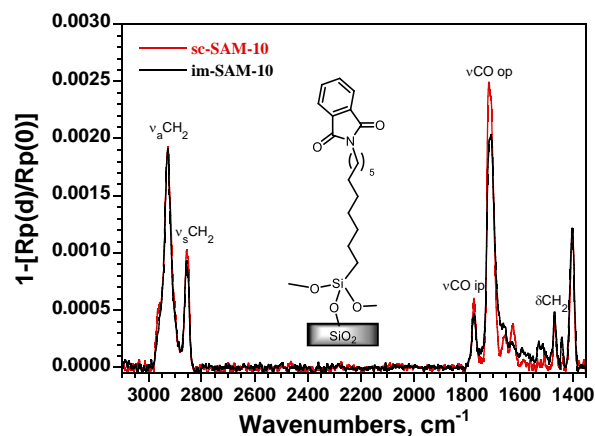


Figure 3 PM-IRRAS spectra of compound **10** grafted onto the SiO₂/Au substrate by spin coating (**sc-SAM-10**) and by the solution immersion method (**im-SAM-10**).

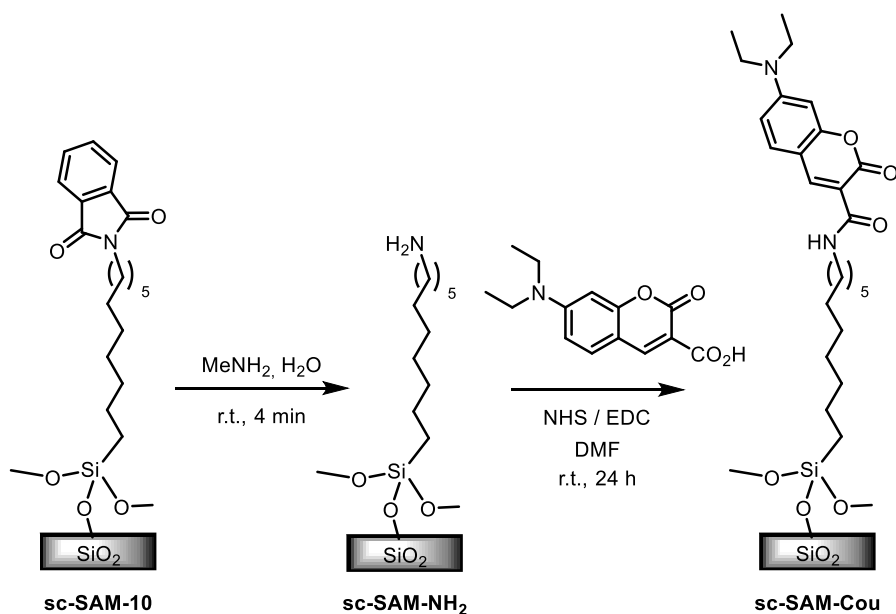
Elaboration of the amine-terminated SAM and evaluation of its reactivity

Then, it appeared important to us to confirm that these SAMs obtained by spin coating are robust and could be reactive for further classical surface modifications. The deprotection of the phthalimide groups of **sc-SAM-10** was performed with 40% aqueous methylamine to provide **SAM-NH₂** (Figure 4a).⁴¹ The PM-IRRAS spectrum of **SAM-NH₂** recorded after the chemical surface modification is reported in Figure 4b. The same results have been obtained starting from **im-SAM-10**. The success of the deprotection was evidenced by the total disappearance of the two bands at 1772 cm⁻¹ and 1710 cm⁻¹, associated to the imide function of the phthalimide terminal group, and the appearance of a new band at 1620 cm⁻¹ associated to the bending vibration of NH₂ groups. The slightly decrease of the intensity of the ν_aCH₂ and ν_sCH₂ bands is certainly related to more vertical orientation of the alkyl chains due to smaller size of the NH₂ terminal group. The increase of the surface's hydrophilicity was confirmed by wettability measurements. Indeed, upon deprotection the contact angle value decreased to reach 48° ± 2° for **SAM-NH₂**. AFM analysis confirmed also the integrity of the monolayer since AFM height images and rms roughness looked like the same before and after deprotection (Figures S3 and S4, Supporting Information).

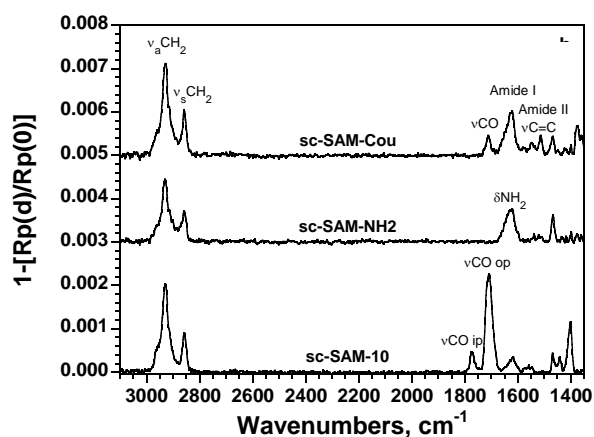
Amine-terminated SAMs are commonly used for the immobilization of molecules onto silica substrates by reacting the amino-terminal groups with various organic functions such as activated carboxylic acids, isocyanates, isothiocyanates, acyl chlorides or sulfonyl chlorides.⁴² Thus, we investigated the reactivity of **SAM-NH₂** towards peptide coupling by PM-IRRAS and fluorescence spectroscopy. To do so, we used 7-(diethylamino)coumarin-3-carboxylic acid as a fluorescent probe with a carboxylic acid group which was first activated with a mixture of carbodiimide and *N*-hydroxysuccinimide (Figure 4a). The fluorescence spectrum of **sc-SAM-Cou** obtained after the reaction of **sc-SAM-NH₂** with the coumarin derivative is shown in Figure 4c. The emission band of the coumarin moiety⁴³ with a maximum at 475 nm was clearly visible which evidenced the presence of reactive amino groups. Moreover, exposed amino groups

display the same accessibility whatever the silanization method applied to elaborate the precursor **SAM-10**. Indeed, similar results were observed when the deprotection / peptide coupling sequence was applied to **im-SAM-10**, including the emission intensity of the resulting **im-SAM-Cou**. The reactivity of **SAM-NH₂** towards peptide coupling was confirmed by PM-IRRAS with the presence of several bands related to the coumarin moiety ($\nu\text{C}=\text{O}$ at 1712 cm^{-1} , $\nu\text{C}=\text{C}$ and δCH at 1515 and 1380 cm^{-1}) and to the amide link (amide I at 1625 cm^{-1} and amide II at 1547 cm^{-1}). Finally, the increase of the intensity of the $\nu_a\text{CH}_2$ and $\nu_s\text{CH}_2$ bands for **sc-SAM-Cou** is certainly related to more tilted/disordered orientation of the alkyl chains due to attachment of the bulky end group.

a)



b)



c)

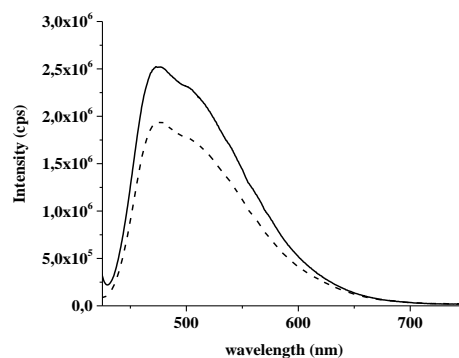


Figure 4 a) Schematic representation of the preparation of **sc-SAM-NH₂** and its reaction via peptide coupling; b) PM-IRRAS spectra of **sc-SAM-Cou**, **sc-SAM-NH₂** and **sc-SAM-10**; c) Fluorescence spectra of **sc-SAM-Cou** (solid line) and **im-SAM-Cou** (dash line).

CONCLUSION

This study demonstrates that the spin coating technique can be considered as a general and advantageous deposition method to prepare smooth and homogeneous SAMs onto silica substrates. We performed successfully the grafting of four silylated coupling agents displaying various molecular structures to afford either alkyl or hydrogen-bonding SAMs with bromine, benzyl or phthalimide terminal groups. PM-IRRAS characterizations, AFM analysis and wettability measurements show that SAMs elaborated by spin coating display the same properties and the same quality as those manufactured with the conventional immersion method. We also evidenced that the covalent grafting of organotrimethoxysilanes by spin coating is robust and that the corresponding functional SAMs can undergo several chemical surface modifications without degradation. Indeed, bromine-terminated SAM was successfully converted into azide-terminated SAM and deprotection of SAM with phthalimide groups led to amine-terminated SAM. Fluorescence measurements confirmed that the exposed amino groups were reactive with a coumarin derivative. In the future, the spin coating technique should attract wide interest as an alternative process for elaborating SAM in ambient conditions since it is simple, easy to handle, reproducible; it requires less solvent and in most cases it allows to significantly decrease the duration of elaboration.

Electronic supplementary information (ESI) available

ESI contains descriptions and data related to the synthesis of silylated coupling agents and their precursors including NMR, IR and mass spectra as well as AFM images of surfaces.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors acknowledge financial support from “Consulat Général de France à Jérusalem” (NAH PhD grant), Bordeaux University and the National Center for Scientific Research (CNRS).

REFERENCES

- (1) Singh, M.; Kaur, N.; Comini, E. The role of self-assembled monolayers in electronic devices. *J. Mater. Chem. C* **2020**, *8*, 3938-3955.
- (2) Carvalho, R. R.; Pujari, S. P.; Gahtory, D.; Vrouwe, E. X.; Albada, B.; Zuilhof, H. Mild Photochemical Biofunctionalization of Glass Microchannels. *Langmuir* **2017**, *33*, 8624-8631.
- (3) Carlos, L. D.; Ferreira, R. A. S.; Bermudez, V. Z.; Ribeiro, S. J. L. Lanthanide-containing light-emitting organic–inorganic hybrids: a bet on the future. *Adv. Mater.* **2009**, *21*, 509-534.
- (4) Zamboulis, A.; Moitra, N.; Moreau, J. J. E.; Cattoen, X.; Man, M.W.C. Hybrid materials: versatile matrices for supporting homogeneous catalysts. *J. Mater. Chem.* **2010**, *20*, 9322-9338.

- (5) Vashist, S. K.; Lam, E.; Hrapovic, S.; Male, K. B.; Luong, J. H. T. Immobilization of Antibodies and Enzymes on 3-Aminopropyltriethoxysilane-Functionalized Bioanalytical Platforms for Biosensors and Diagnostics. *Chem. Rev.* **2014**, *114*, 11083-1130.
- (6) Jonkheijm, P.; Weinrich, D.; Schröder, H.; Niemeyer, C.M.; Waldmann, H. Chemical strategies for generating protein biochips. *Angew. Chem. Int. Ed.* **2008**, *47*, 9618-9647.
- (7) Samanta, D.; Sarkar, A. Immobilization of bio-macromolecules on self-assembled monolayers: methods and sensor applications. *Chem. Soc. Rev.* **2011**, *40*, 2567-2592.
- (8) Wong, L.S.; Khan, F.; Micklefield, J. Selective Covalent Protein Immobilization: Strategies and Applications. *Chem. Rev.* **2009**, *10*, 4025-4053.
- (9) Fournel, F.; Baco, E.; Mamani-Matsuda, M.; Degueil, M.; Bennetau, B.; Moynet, D.; Mossalayi, D.; Vellutini, L.; Pillot, J.-P.; Dejous, C.; Rebière, D. Love wave biosensor for real-time detection of okadaic acid as DSP phycotoxin. *Sens. Actuator B-Chem.* **2012**, *170*, 122-128.
- (10) Dinh, D.H.; Pascal, E.; Vellutini, L.; Bennetau, B.; Rebière, D.; Dejous, C.; Moynet, D.; Belin, C.; Pillot, J.-P. Novel optimized biofunctional surfaces for Love mode surface acoustic wave based immunosensors. *Sens. Actuator B-Chem.* **2010**, *146*, 289-296.
- (11) Pujari, S.P.; Scheres, L.; Marcelis, A.T.M.; Zuilhof, H. Covalent Surface Modification of Oxide Surfaces. *Angew. Chem. Int. Ed.* **2014**, *53*, 6322-6356.
- (12) Onclin, S.; Ravoo, B. J.; Reinhoudt, D. N. Engineering silicon oxide surfaces using self-assembled monolayers. *Angew. Chem. Int. Ed.* **2005**, *4*, 6282-6304.
- (13) Wang, L.; Schubert, U. S.; Hoeppeener, S. Surface chemical reactions on self-assembled silane based monolayers. *Chem. Soc. Rev.* **2021**, *50*, 6507-6540.
- (14) Escorihuela, J.; Pujari, S. P.; Zuilhof, H. Organic Monolayers by B(C₆F₅)₃-Catalyzed Siloxanation of Oxidized Silicon Surfaces. *Langmuir* **2017**, *33*, 2185-2193.
- (15) Lee, T. -J.; Chau, L. -K.; Huang, C. -J. Controlled Silanization: High Molecular Regularity of Functional Thiol Groups on Siloxane Coatings. *Langmuir* **2020**, *36*, 5935-5943.
- (16) Vega, A.; Thissen, P.; Chabal, Y.J. Environment-Controlled Tethering by Aggregation and Growth of Phosphonic Acid Monolayers on Silicon Oxide. *Langmuir* **2012**, *28*, 8046-8051.
- (17) Hanson, E. L.; Schwartz, J.; Nickel, B.; Koch, N.; Danisman, M.F. Bonding Self-Assembled, Compact Organophosphonate Monolayers to the Native Oxide Surface of Silicon. *J. Am. Chem. Soc.* **2003**, *125*, 16074-16080.
- (18) Dubey, M.; Weidner, T.; Gamble, L. J.; Castner, D. G. Structure and Order of Phosphonic Acid-Based Self-Assembled Monolayers on Si(100). *Langmuir* **2010**, *26*, 14747-14754.
- (19) Lee, A. W. H.; Gates, B. D. Rapid Covalent Modification of Silicon Oxide Surfaces through Microwave-Assisted Reactions with Alcohols. *Langmuir* **2016**, *32*, 7284-7293.
- (20) Barness, Y.; Gershevitz, O.; Sekar, M.; Sukenik, C.N. Functionalized Silanes for the Preparation of Siloxane-Anchored Monolayers. *Langmuir* **2000**, *16*, 247-251.
- (21) Silberzan, P.; Léger, L.; Ausserré, D.; Benattar, J. J. Silanation of silica surfaces. A new method of constructing pure or mixed monolayers. *Langmuir* **1991**, *7*, 1647-1651.
- (22) Meillan, M.; Ramin, M. A.; Buffeteau, T.; Marsaudon, S.; Odorico, M.; Chen, S.-w. W.; Pellequer, J.-L.; Degueil, M.; Heuzé, K.; Vellutini, L.; Bennetau, B. Self-assembled monolayer for AFM measurements of Tobacco Mosaic Virus (TMV) at the atomic level. *RSC Adv.* **2014**, *4*, 11927-11930.
- (23) Dong, J.; Wang, A.; Ng, K. Y. S.; Mao, G. Self-assembly of octadecyltrichlorosilane monolayers on silicon-based substrates by chemical vapor deposition. *Thin Solid Films* **2006**, *515*, 2116-2122.
- (24) Lowe, R. D.; Pellow, M. A.; Stack, T. D. P.; Chidsey, C. E. D. Deposition of Dense Siloxane Monolayers from Water and Trimethoxyorganosilane Vapor. *Langmuir* **2011**, *27*, 9928-9935.

- (25) Vos, R.; Rolin, C.; Rip, J.; Conard, T.; Steylaerts, T.; Cabanilles, M. V.; Levrie, K.; Jans, K.; Stakenborg, T. Chemical Vapor Deposition of Azidoalkylsilane Monolayer Films. *Langmuir* **2018**, *34*, 1400-1409.
- (26) Pellow, M. A.; Stack, T. D.; Chidsey, C. E. D. Squish and CuAAC: Additive-Free Covalent Monolayers of Discrete Molecules in Seconds. *Langmuir* **2013**, *29*, 5383-5387.
- (27) Niehaus, J. C.; Hirtz, M.; Brinks, M. K. Studer, A. Fuchs, H.; Chi, L. Patterning of Functional Compounds by Multicomponent Langmuir–Blodgett Transfer and Subsequent Chemical Modification. *Langmuir* **2010**, *26*, 15388-15393.
- (28) Kojio, K.; Takahara, A.; Omote, K.; Kajiyama, T. Molecular Aggregation State of n-Octadecyltrichlorosilane Monolayers Prepared by the Langmuir and Chemisorption Methods. *Langmuir* **2000**, *16*, 3932-3936.
- (29) Devynck, M.; Tardy, P.; Wantz, G.; Nicolas, Y.; Hirsch, L. Organic field-effect transistor with octadecyltrichlorosilane (OTS) self-assembled monolayers on gate oxide: effect of OTS quality. *Eur. Phys. J. Appl. Phys.* **2011**, *56*, 34106-34112.
- (30) Xiao, Z.; Cai, C.; Mayeux, A.; Milenkovic, A. The First Organosiloxane Thin Films Derived from SiCl₃-Terminated Dendrons. Thickness-Dependent Nano- and Mesoscopic Structures of the Films Deposited on Mica by Spin-Coating. *Langmuir* **2002**, *18*, 7728-7739.
- (31) Praveen, S. G.; Binay, J.; Kumaran, J. T. T.; Bansal, C.; Audline Jini, M. N.; Jayakumar, V.S. Rotation dependent Si hyperconjugation in self assembly material p-tolytrichlorosilane (PTCS) and formation of SAM. *J. Mol. Structure* **2014**, *1064*, 81-87.
- (32) Ito, Y.; Virkar, A. A.; Mannsfeld, S.; Hak Oh, J.; Toney, M.; Locklin, J.; Bao, Z. Crystalline Ultrasoother Self-Assembled Monolayers of Alkylsilanes for Organic Field-Effect Transistors. *J. Am. Chem. Soc.* **2009**, *131*, 9396-9404.
- (33) Mousli, Y.; Rouvière, L.; Traboulsi, I.; Hunel, J.; Buffeteau, T.; Heuzé, K.; Vellutini, L.; Genin, E. Hydrosilylation of Azide-Containing Olefins as a Convenient Access to Azidoorganotrialkoxysilanes for Self-Assembled Monolayer Elaboration onto Silica by Spin Coating. *ChemistrySelect* **2018**, *3*, 7333-7339.
- (34) Al-Hajj, N.; Mousli, Y.; Miche, A.; Humblot, V.; Hunel, J.; Heuzé, K.; Buffeteau, T.; Genin, E.; Vellutini, L. Influence of the grafting process on the orientation and the reactivity of azide-terminated monolayers onto silica surface. *Appl. Surf. Sci.* **2020**, *527*, 146778-146785.
- (35) Buffeteau, T.; Desbat, B.; Turllet, J.-M. Polarization Modulation FT-IR Spectroscopy of Surfaces and Ultra-thin Films: Experimental Procedure and Quantitative Analysis. *Appl. Spectrosc.* **1991**, *45*, 380-389.
- (36) M. A. Ramin, G. Le Bourdon, N. Daugey, B. Bennetau, L. Vellutini, T. Buffeteau, PM-IRRAS Investigation of Self-Assembled Monolayers Grafted onto SiO₂/Au Substrates, *Langmuir*, 2011, **27**, 6076-6084.
- (37) . Buffeteau, B. Desbat, D. Blaudez, J.-M. Turllet, Calibration Procedure to Derive IRRAS Spectra from PM-IRRAS Spectra, *Appl. Spectrosc.*, 2000, **54**, 1646-1650.
- (38) Balachander, N.; Sukenik, C.N. Monolayer transformation by nucleophilic substitution: Applications to the creation of new monolayer assemblies. *Langmuir* **1990**, *6*, 1621-1627.
- (39) Ramin, M. A.; Le Bourdon, G.; Heuzé, K.; Degueil, M.; Belin, C.; Buffeteau, T.; Bennetau, B.; Vellutini, L. Functionalized Hydrogen-Bonding Self-Assembled Monolayers Grafted onto SiO₂ Substrates. *Langmuir* **2012**, *28*, 17672-17680.
- (40) Ramin, M. A.; Le Bourdon, G.; Heuzé, K.; Degueil, M.; Buffeteau, T.; Bennetau, B.; Vellutini, L. Epoxy-Terminated Self-Assembled Monolayers Containing Internal Urea or Amide Groups. *Langmuir* **2015**, *31*, 2783-2789.

- (41) Siurdyban, E.; Brotin, T.; Heuzé, K.; Vellutini, L.; Buffeteau, T. Grafting of cryptophane derivatives onto SiO₂/Au and Au Substrates. *Langmuir* **2014**, *30*, 14859-14867.
- (42) Flink, S.; van Veggel, F. C. J. M.; Reinhoudt, D. N. Functionalization of self-assembled monolayers on glass and oxidized silicon wafers by surface reactions. *J. Phys. Org. Chem.* **2001**, *14*, 407-415.
- (43) Maity, B.; Chatterjee, A.; Seth, D. The photophysics of 7-(diethylamino)coumarin-3-carboxylic acid N-succinimidyl ester in reverse micelle: excitation wavelength dependent dynamics. *RSC Adv.* **2014**, *4*, 3461-3471.

“ For Table of Content Only”

