Viable Synthetic Route for a Luminescent Porphyrin Monolayer Covalently Assembled on a Molecularly Engineered Si(100) Surface

Antonino Gulino,* Fabio Lupo, Guglielmo G. Condorelli,* Placido Mineo, and Ignazio Fragalà

Dipartimento di Scienze Chimiche, Università di Catania and I.N.S.T.M. UdR di Catania Viale Andrea Doria 6, 95125 Catania, Italy

Received May 29, 2007. Revised Manuscript Received July 31, 2007

A three-step strategy to covalently anchor 5,10,15,20-tetrakis(hydroxyphenyl)porphyrin molecules on Si(100) substrates was developed. It consists of the functionalization of the Si(100) surface by the grafting of 10-undecylenic acid methyl ester on the H-terminated silicon surface, followed by the ester hydrolysis and, finally, by the covalent assembly of the tetrakis(hydroxyphenyl)porphyrin. The obtained system was characterized by monochromated angle-resolved X-ray photoelectron spectra and atomic force microscopy measurements. Results indicated the covalent linkage of the porphyrin molecules to the functionalized substrate surface. Moreover, both XPS and AFM measurements suggest that the porphyrins bind the surface in a vertical fashion. The monolayer optical behavior was studied by photoluminescence measurements at room temperature.

Introduction

Engineering of inorganic surfaces by covalent bonding of organic molecules represents an interesting approach to the synthesis of hybrid inorganic/organic nanomaterials.[1−12] The use of the conducting Si(100)[13−22] or other[23−26] substrates is potentially interesting from the perspective of optoelectronic device fabrication that can be easily integrated within electronic circuits. Porphyrin thin films have been extensively studied, due to their interesting electrical and optical properties.[16] These thin films are generally obtained by sublimation,[27] spin-coating,[28,29] or by the Langmuir−Blodgett (LB) technique.[30] With these techniques the molecule organization within the film is difficult to control. Moreover, the resulting films are soluble in organic solvents. Recently, porphyrin monolayers were also obtained by self-assembly.[12,24,26,31,32] This simple method relies on the covalent anchoring of the macrocycles on various substrates. Thus, high control on the molecule organization within the monolayer can be obtained.[25]

* Corresponding authors. Fax: +39-095-580138. E-mail: agulino@dipchi.unict.it (A.G.).

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10.1021/cm071450u CCC: $37.00
Published on Web 09/13/2007

Well-organized porphyrin molecules, covalently anchored to silicon substrates, can also be used to build molecular-based information storage materials.[13−17,22] In fact, they behave as redox-active molecules, whose redox potentials can be tuned through synthetic design.[13−17,22] Moreover, when attached to an electroactive surface, information can be stored in the discrete redox states of the molecules.[13−17,22] It has been reported that porphyrin-based information-storage elements exhibit charge-retention times that are long (minutes) compared with those of the semiconductor elements in dynamic random access memory (tens of milliseconds).[22] Collectively, these porphyrin properties afford the possibility of increased memory density (via multibit information storage) with decreased power consumption (low potentials and long charge-retention times).[13−17,22]

Several recent studies on grafting of organic molecules on silicon surfaces focused on the Si(111) substrate because of the simple chemical etching procedure available to obtain atomically flat and chemically well-defined surfaces.[33] Moreover, it has also been reported that it is possible to produce relatively flat Si(100) surfaces, predominantly SiH_2-terminated, even though SiH and SiH_3 groups are present.[34]

Among the various covalent bonding modes of organic molecules to silicon, hydrosilation of molecules with multiple bonds on hydrogen-terminated surfaces appears the best suited for the largest potential applications.[35]

Recently, it has been shown that porphyrins can be covalently attached to silica platforms to form high quality sensor devices.[36−42] Herein, we expand our previous investigations[36,37,38b,39−41] to show a new approach to obtain porphyrin-based monolayers covalently bonded to conducting Si(100) surfaces, potentially suited for use in electronic devices.

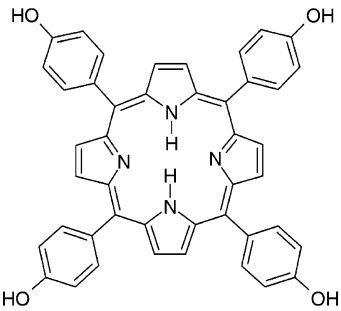

Figure 1. Schematic draw of 5,10,15,20-tetrakis(hydroxyphenyl)porphyrin (P).

In this context, we focused our interest on the grafting of the 5,10,15,20-tetrakis(hydroxyphenyl)porphyrin (called $P(OH)_4$, Figure 1). The resulting porphyrin monolayers have been characterized via angle resolved X-ray photoelectron spectroscopy (AR-XPS) and atomic force microscopy (AFM) and luminescence measurements.

Experimental Section

All chemicals, unless otherwise noted, were commercially available (Sigma-Aldrich) and used as received. Solvents for substrate cleaning were distilled. 1-Decene for monolayer preparation was distilled under reduced pressure over Na metal. The 10-undecylenic acid methyl ester was synthesized according to the method reported by Sieval et al.[43] In particular, a mixture of 10-undecylenic acid (10 g, 54 mmol), 65 mL of methanol, and 0.14 mL of sulfuric acid was refluxed for 3 h. The methanol excess was removed in a vacuum, and the resulting material was dissolved in ether. The product was distilled under vacuum to obtain a transparent liquid.

Monolayer Preparation (Scheme 1**).** Ten milliliters of pure 10-undecylenic acid methyl ester ($CH_2{=}CH(CH_2)_8COOCH_3$) was placed in a small, three-necked flask fitted with a nitrogen inlet and a condenser. The liquid was deoxygenated with dry N_2 for 1 h. The Si(100) substrate was first cleaned with "piranha" solution (concentrated H_2SO_4:35% H_2O_2 70:30 v/v) at room temperature for 12 min, rinsed in double distilled water for 2 min, etched in 2.5% hydrofluoric acid for 90 s, washed with double distilled water for 10 s, dried with prepurified N_2, and immediately placed in the alkene-containing flask. This system was then refluxed at 170 °C for 2 h, under slow N_2 bubbling to prevent bumping. After cooling to room temperature, the substrate was removed from the flask and sonicated in dichloromethane for 10 min. Hydrolysis of the Si(100)-supported 10-undecylenic acid methyl ester was performed according to a method reported by Strother et al.[44] Briefly, grafted surfaces were dipped in a solution of 0.285 g of potassium *tert*-butoxide in 10 mL of DMSO for 30 s at room temperature, followed by rinsing with a 0.1 M HCl solution and, finally, washing with water.

Then, the Si(100)-supported 10-undecylenic acid substrate (Si(100)$-(CH_2)_{10}COOH$) was immersed in a 8.7×10^{-4} M water solution of the present porphyrin sodium salt [$P(ONa)_4$] at room

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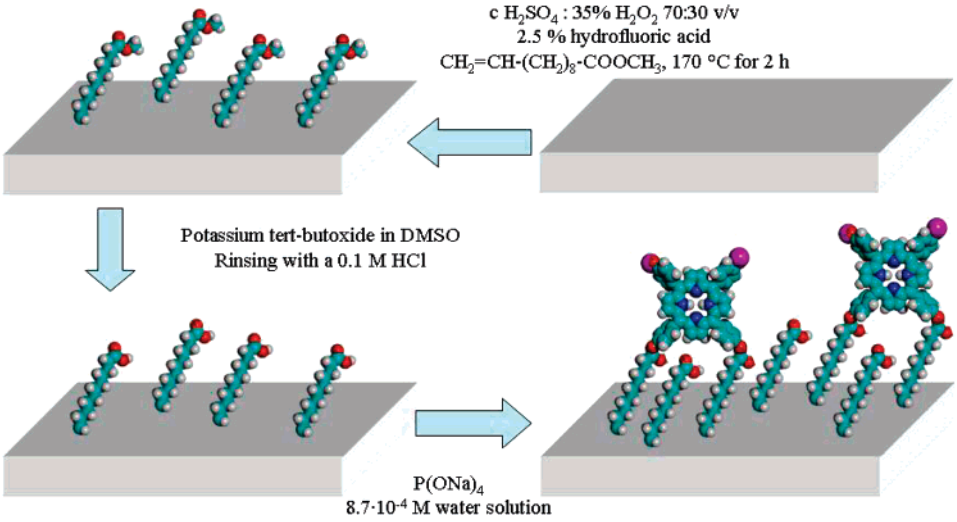
Scheme 1



temperature under stirring for 12 h. Next, substrates bearing the porphyrin covalently assembled monolayer (Si(100)−P-CAM) were repeatedly sonicated and alternately washed with water and 2-propanol to remove any residual unreacted porphyrin. After that, substrates were washed with a pH 9 water solution in order to remove any eventual ionically (noncovalent) bounded species and, finally, washed again with double distilled water. No reaction has been observed when anhydrous dimethyl sulfoxide (DMSO) was used as solvent.

Angle resolved X-ray photoelectron spectra (AR-XPS) of the Si(100)−P-CAM were measured at two different takeoff angles, relative to the surface plane, (10°, 45°) with a PHI 5600 Multi Technique System, which offers a good control of the electron off-take angle (base pressure of the main chamber 2×10^{-10} Torr).[45,46] The acceptance angle of the analyzer and the precision of the sample holder concerning the takeoff angle are ±3° and ±1°, respectively.[38b] The spectrometer is equipped with a dual anode X-ray source, a spherical capacitor analyzer (SCA) with a mean diameter of 279.4 mm, and an electrostatic lens system Omni focus III. Samples were mounted on Mo stubs. Spectra were excited with monochromatic Al Kα radiation. The XPS peak intensities were obtained after Shirley background removal.[47] No relevant charging effect has been observed. Freshly prepared samples were quickly transferred to the XPS main chamber. Experimental uncertainties in binding energies lie within ±0.28 eV.[48] Some spectra were deconvoluted by fitting the spectral profiles with a series of symmetrical Gaussian envelopes after subtraction of the background. The agreement factor, $R = [\sum(F_o - F_c)^2/\sum-(F_o)^2]^{1/2}$, after minimization of the function $\sum(F_o - F_c)^2$ converged to R values ≤ 0.04.

Atomic force microscopy (AFM) measurements were performed with a Solver P47 NTD-MDT instrument in semicontact mode (resonance frequency 150 Hz).

Room-temperature photoluminescence (PL) spectra were obtained with a SPEX Fluorolog 111 instrument equipped with a xenon lamp (450 W), operating in the 200−800 nm range, with two monochromators. The monolayer was photoexcited with a 425 nm line beam. The emission was recorded at 90° with respect to the exciting line beam.

Results and Discussion

The preparation of $P(OH)_4$ molecules covalently assembled on silicon surfaces required a three-step procedure (Scheme 1): (i) grafting of the undecylenic acid methyl ester on H-terminated Si(100) surfaces via thermal hydrosilylation, (ii) hydrolysis of the ester, and (iii) reaction of a porphyrin sodium salt water solution with the Si(100)-supported 10-undecylenic acid substrate.

We are aware that in water solution the reaction between a carboxylic acid and sodium phenolate does not occur. Nevertheless, two different reaction mechanisms can be hypothesized to rationalize the observed reaction (vide infra) in the present heterogeneous system (solid−liquid interphase). (1) The carboxylic acid functionalities on the Si surface immersed in water give an extremely concentrated acidic surface that can give rise to self-protonated $-COOH_2^+$ surface groups. In water, the porphyrin sodium phenolate dissociates to give a porphyrin phenolate group. Therefore, an acid-catalyzed esterification reaction between $-COOH_2^+$ and the anionic porphyrin phenolate can occur by nucleophilic substitution. (2) The equilibrium reaction porphyrin phenolate + R−COOH = porphyrin−OOCR + OH^- in water can be unbalanced toward the right because of the very low local (on the surface) OH^- concentration. In fact, the concentration of OH^- groups originating from the reaction can be evaluated to be lower than that coming from the water self-dissociation. Both hypotheses require the presence of a water layer on the substrate surface and, therefore, agree well with the fact that no reaction has been observed in anhydrous DMSO.

These overall observations suggest that porphyin molecules are covalently attached to the substrate via the undecylenic acid moiety. The obtained new porphyrin covalently assembled monolayers are robust and strongly adhere to the substrate surface, as they cannot be removed by repeated sonication, basic solution washing, nor by the "Scotch tape decohesion" test, as evidenced by both XPS and luminescence measurements.

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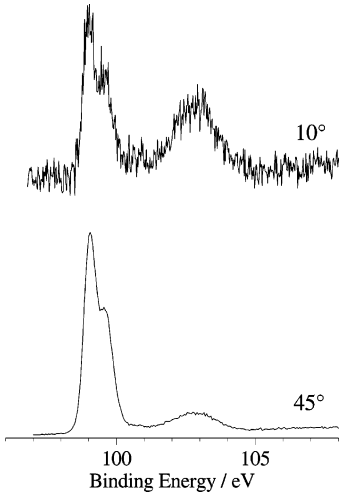

Figure 2. Monocromated Al Kα excited XPS of Si(100)−P-CAM in the Si 2p energy region at 10° and 45° electron takeoff angles.

Table 1. XPS Atomic Concentration Analysis of the Si(100)−P-CAM

PTA,[a] deg	Si 2p	O 1s	C 1s	N 1s
45	20.7 (Si) + 5.2 (SiO_2) = 25.9	25.8	47.4	0.9
10	8.6 (Si) + 6.3 (SiO_2) = 14.9	20.2	63.4	1.5

[a] PTA = photoelectron takeoff angle.

Molecular monolayer characterization of the Si(100)−P-CAM was carried out with X-ray photoelectron spectroscopy. This technique is ideal, since it allows high vertical resolution and gives information on the bonding states of the grafted molecules by the analysis of angle-resolved measurements.[36−40,49]

Table 1 collects XPS atomic concentration data of a prototypical Si(100)−P-CAM at 45° and 10° photoelectron takeoff angles (PTA), once the relevant atomic sensitivity factors have been accounted for.[50] On the basis of XPS results,[49] it is possible to estimate the surface coverage with porphyrin molecules, 2.5×10^{13} molecules/cm^2. This value is similar to those already obtained for SiO_2-supported porphyrin monolayers.[40,41]

No fluorine signal was observed. Moreover, there is evidence of a decrease of both Si and O peaks, while the C signal significantly increases, on decreasing of the PTA. The N peak shows a moderate increase only.

In particular, the whole Si 2p signal goes from 25.9% at 45° to 14.9% at 10° photoelectron takeoff angles (Table 1). Two features are always evident (Figure 2). The 2p doublet at 99.0 ($2p_{3/2}$) and 99.6 ($2p_{1/2}$) eV,[20,51] consistent with the presence of Si, whose atomic concentration goes from 20.7% at 45° to 8.6% at 10°, and the broad band at 103.0 eV,[52−54] consistent with the presence of some SiO_2, whose atomic concentration goes from 5.2% at 45° to 6.3% at 10°.

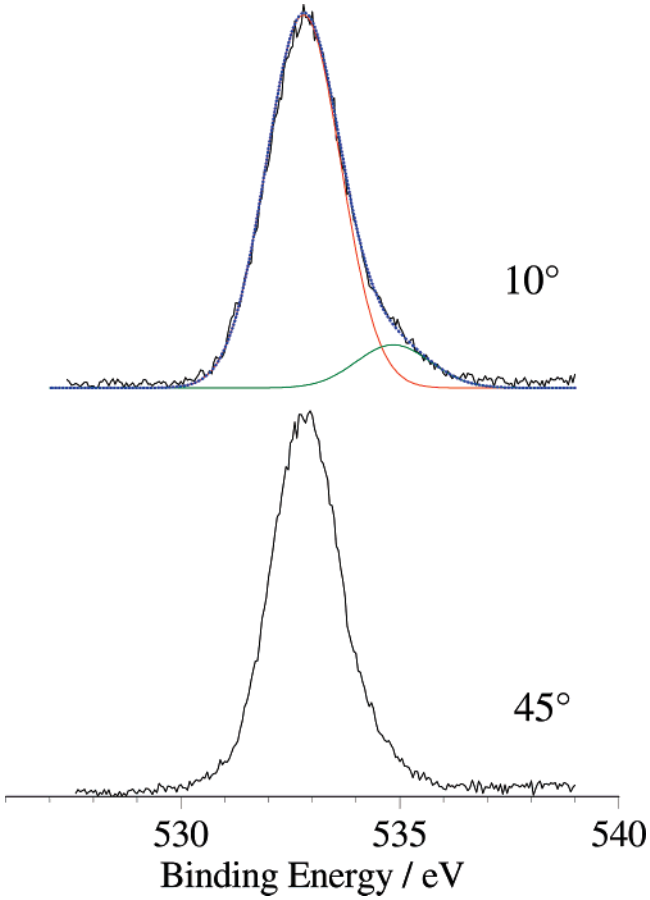

Figure 3. Monocromated Al Kα excited XPS of Si(100)−P-CAM in the O 1s energy region at 10° and 45° electron takeoff angles.

Moreover, the 2:1 spin−orbit doublet, at lower binding energy, shows a separation of 0.6 eV, well-tuned with that expected for a Si(100) substrate.[20,51] The decreasing intensity behavior of the Si 2p signal, on decreasing the photoelectron takeoff angle, is mainly due to the falloff of the Si(100) component. The presence of some substrate surface oxidation is not unexpected for the ester-fuctionalizated Si(100) surface after hydrolysis and functional molecule linkage (in water media) steps and was already reported for a similar system.[55]

Analogously, the O 1s signal suffers an intensity decrease on going from 45° (25.8%) to 10° (20.2%) (Table 1). It therefore transpires that this signal is largely due to the SiO_2 substrate phase rather than to the porphyrin oxygen. Figure 3 shows a main peak at 533.0 eV with a high energy (534.8 eV) shoulder, evident at 10° takeoff angle. This shoulder ($^1/_{15}$ of the intensity of the main peak) accounts for the oxygen of the C═O group of the esteric functionality[51] of the −COOP feature.

Figure 4 compares C 1s photoelectron spectra of Si-supported undecylenic acid (left inset), Si(100)−P-CAM) (main figure), and acetylated Si(100)−P-CAM (right inset; vide infra). The C1s band of the acid (left inset) consists of two main components: the first centered at 285.0 eV is due to the aliphatic backbone and the second at 289.6 eV is due

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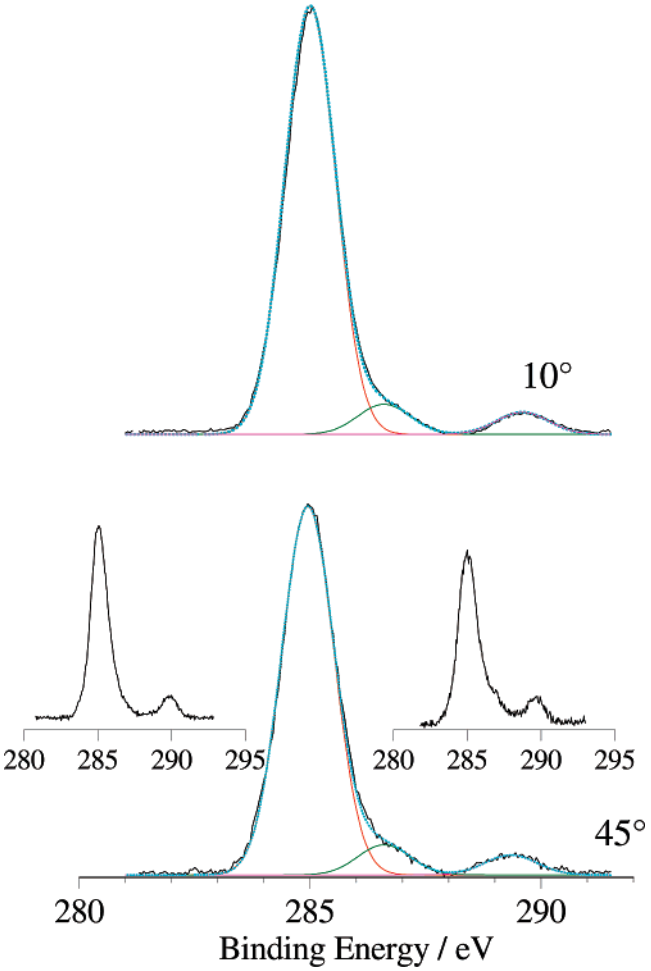

Figure 4. Monocromated Al Kα excited XPS of Si(100)−P-CAM in the C 1s energy region at 10° and 45° electron takeoff angles. The dashed line, superimposed to the experimental profile, refers to the sum of the Gaussian components. Left inset: spectrum of the Si(100)-supported undecylenic acid. Right inset: spectrum of the Si(100)−P-CAM after reaction with acetic anhydride.

to the carbon of the COOH group.[56] Photoelectron spectra of Si(100)−P-CAM in the C 1s region (main Figure 4) consist of three main components. The first, centered at 285.0 eV, is due to both aliphatic and aromatic backbones (hereafter referred to as C^0).[57−58] The shoulder at 286.6 eV, in tune with literature data,[50,59−61] is due to the carbon center of the porphyrin phenyl ring bonded to one oxygen atom and to the −C═N porphyrin groups. Finally, the highest binding energy component at 289.4 eV is due to the −COOP and unreacted −COOH groups, where P represents the porphyrin. Note that the relative intensity (with respect to the C^0 component) of this band is much lower compared to the Si-supported acid, accounting for the increased number of carbon atoms due to the presence of the porphyrin backbone.

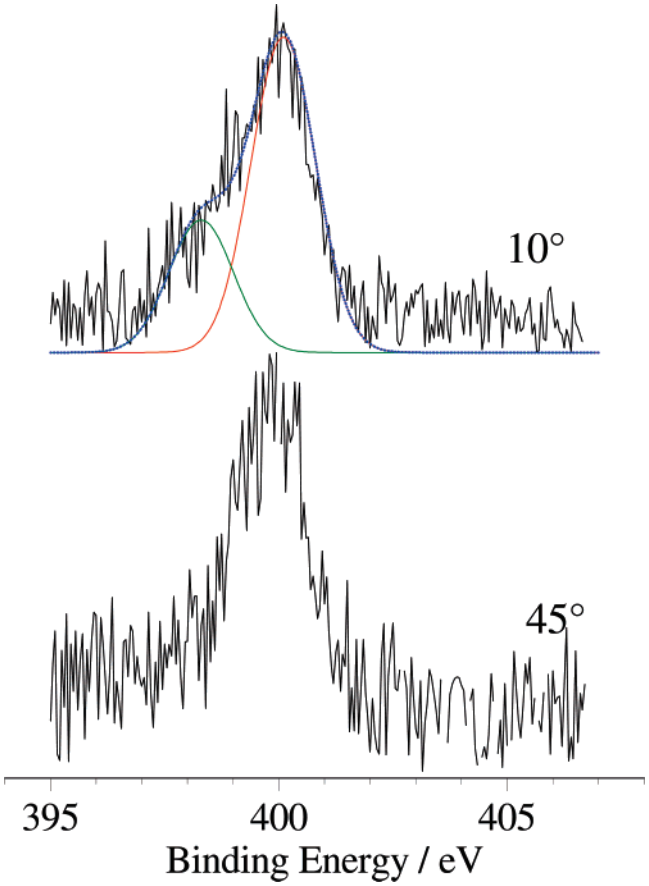

Figure 5. Monocromated Al Kα excited XPS of Si(100)−P-CAM in the N 1s energy region at 10° and 45° electron takeoff angles. The dashed line, superimposed to the experimental profile, refers to the sum of the Gaussian components.

Worthy of note, the whole carbon atomic concentration significantly increases from 47.4% (at 45°) to 63.4% (at 10°), as expected for the upper layer nature of the signal (Table 1).

Finally, the nitrogen atomic concentration shows a significant increase upon decreasing the electron takeoff angle from 0.9% (at 45°) to 1.5% (at 10°) (Table 1). The N 1s spectra (Figure 5) show a peak with a shoulder at 400.1 and 398.2 eV, respectively. These features account for the two kinds of nitrogen in the free porphyrin base.[26,32,57,58,62,63] According to already reported studies on similar porphyrin systems, the lower/higher BE intensity ratio is about 1:3.[37−42,49]

In order to obtain suited reference for the N 1s feature of the porphyrin sodium salt, some test samples consisting of Si(100) substrates immersed in some 10^{-4} M C_2H_5OH porphyrin solutions with identical volumes of 1, 2, 3, or 4 × 10^{-4} M NaOH solutions were analyzed. XPS results always show N 1s spectra with two components having an intensity ratio ∼1:3, in the analyzed takeoff angle range.

Further experiments were made to rule out either any possible physisorption or alternative Si−O−porphyrin sur-

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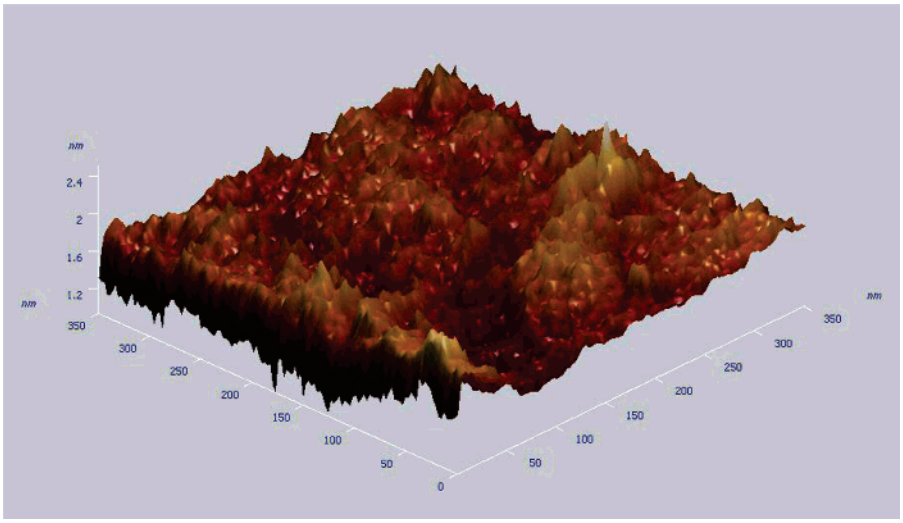

Figure 6. Representative AFM image of the Si(100)−P-CAM.

face grafting.[64] Both a hydrophilic SiO_2 and a hydrophobic undecylenic acid methyl ester terminated surfaces were exposed to a 8.7×10^{-4} M $P(ONa)_4$ water solution and then rinsed, according to the procedures adopted for Si(100)−P-CAM preparation. No $P(OH)_4$ sticking was detected in XPS spectra on both Si−OH and methyl ester terminated surface, thus indicating that physisorption does not occur. On the other hand, electrostatic linkage of these water-soluble porphyrin molecules on the acid-terminated silicon surface can be similarly ruled out, since they cannot be removed by repeated sonication in water nor by basic washing. Moreover, the surface coverage estimated on the basis of XPS results (2.5×10^{13} molecules/cm^2, vide supra) itself helps to rule out any possible physisorption. In fact, the area available on the substrate (footprint) for the porphyrin 10-undecilenic acid molecular assembly is about 2 times larger than the assembly size. Finally, eventual ionic bounded species should give additional XPS peaks at higher binding energies. None of them has been observed in present Si(100)−P-CAMs.

In summary, the XPS technique is very useful to study monolayers since it provides chemical information that is unique and not available with many other spectroscopic techniques.

Surface morphologies of Si(100)−P-CAM were obtained by atomic force microscopy (AFM) measurements.

Figure 6 shows a representative AFM image of the Si-(100)−P-CAM. The obtained average peak-to-peak R_{max} is equal to 0.67 nm with a 1.11 Å mean roughness.

Molecular mechanics force field calculations (MM+ method) performed on this porphyrin molecule covalently bonded to the 10-undecilenic acid give an assembly length of 31.9 Å. AFM measurements do not have enough lateral resolution to show the arrangement of a single molecule on the substrate. Therefore, in order to further investigate the thickness of the Si(100)−P-CAM, atomic force lithography using the AFM tip was performed (Figure 7). Thus, grafted molecules were removed along straight lines by rastering the surface with the AFM tip under a suitable constant force. The obtained scratch depth is about 30 Å and corresponds to the size of the porphyrin almost linearly bonded to the 10-undecilenic acid methyl ester assembly (31.9 Å) (Scheme 1). All these observations should be considered only reasonable estimations. In fact, the real resolution of this technique and the reliability of the MM+ results should be also taken into account. Besides, the porphyrin in the porphyrin 10-undecilenic acid molecular assembly can rotate around different bonds, thus allowing adjacent porphyrin molecules to interact together.[65]

In addition, in order to investigate on the number of binding sites (−OH groups) involved in the substrate grafting by the porphyrin molecule that, in turn, determines the porphyrin geometry adopted with respect to the substrate surface, a Si(100)−P-CAM was dipped into acetic anhydride for 1 h at 60° followed by repeated rinsing in double distilled water and drying under a nitrogen stream. This procedure should be effective in transforming the remaining −OH porphyrin groups, not involved in the grafting, in $P-OCOCH_3$ functionalities. In addition, the washing procedure with water should hydrolyze the eventual mixed anhydride due to the presence of unreacted −COOH groups.

It is evident that the XPS band at 289.4 is more intense in both Si-supported acid (left Inset of Figure 4) and in acetylated Si(100)−P-CAM (right inset of Figure 4) with respect to the Si(100)−P-CAM (main Figure 4). XPS atomic concentration results indicated a 100% increase in the C 1s band, at 289.4 eV in acetylated Si(100)−P-CAM, with respect to that of the Si(100)−P-CAM. Taking into account the presence of COOP moieties and unreacted undecylenic −COOH functionalities, both somewhat buried by the porphyrin molecules, this relevant signal increase mainly indicates the formation of topmost $P-OOCCH_3$ ester functionalities (right inset of Figure 4). This result confirms the

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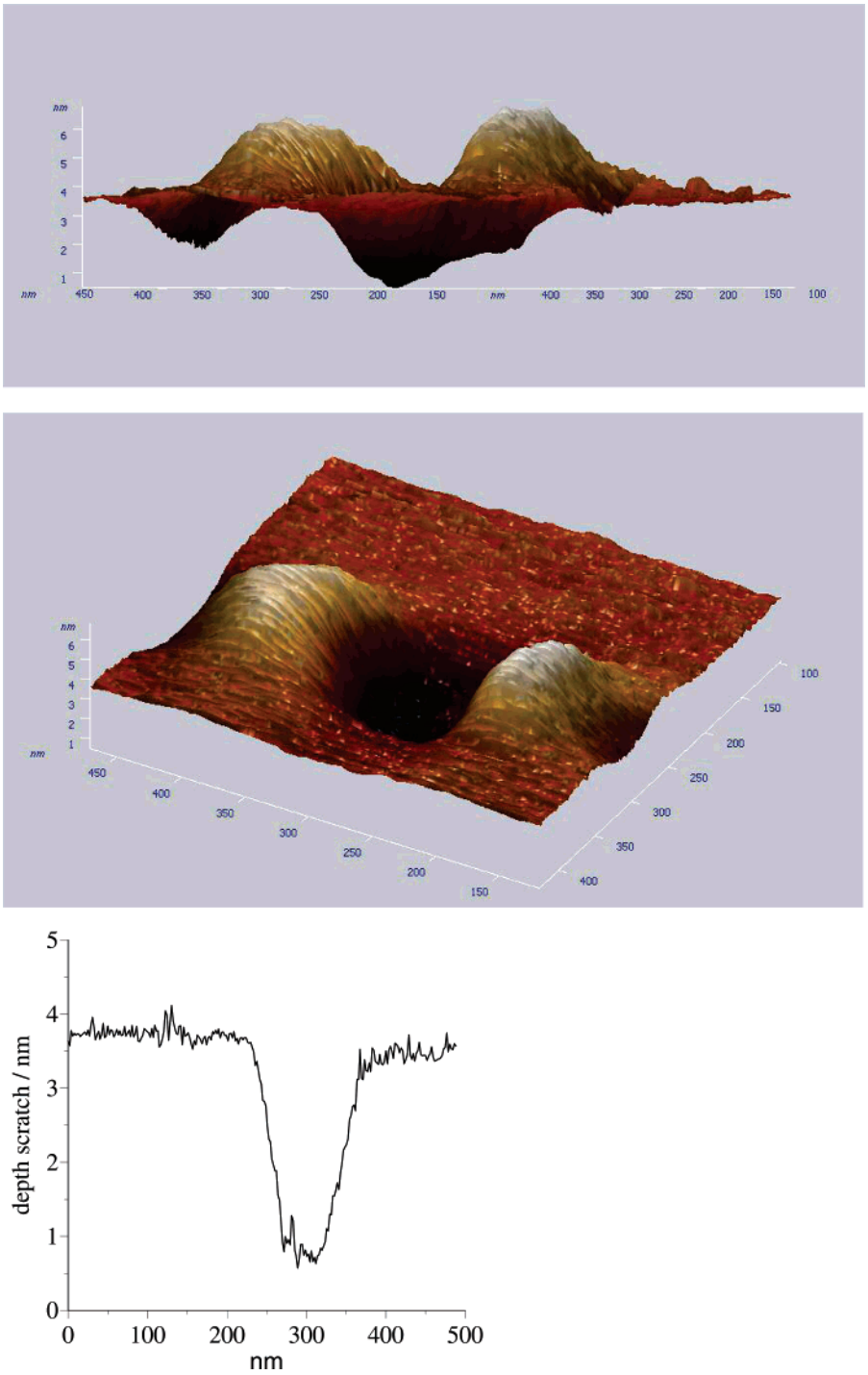

Figure 7. AFM image of the (a) scratch depth section, (b) scratch depth, and (c) 2D scratch size.

obtained AFM depth, indicating that the $P(OH)_4$ bind the surface in a vertical fashion with one or two porphyrin OH groups involved in the substrate grafting. Then, the remaining OH groups of the $P(OH)_4$ molecule undergo the esterification process with acetic anhydride.

Finally, preliminary luminescence measurements carried out on this monolayer show a promising behavior. In fact, Figure 8 shows a representative PL emission spectrum ($\lambda_{exc} = 425$ nm) of the Si(100)−P-CAM. Two well-resolved PL emissions at 658 and 701 nm are evident and well-tuned with already reported measurements on both solutions and thin films.[66−71] Moreover, this result well matches an already reported study on a porphyrin monolayer assembled on a transparent, insulating SiO_2 substrate.[36] The

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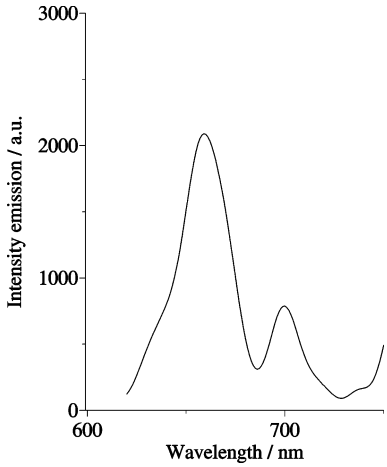

Figure 8. Representative photoluminescence ($\lambda_{exc} = 425$ nm) spectrum of the Si(100)−P-CAM in air.

luminescent behavior presently observed opens new insight in this field, since this porphyrin monolayer is covalently assembled on a conducting Si(100) surface. Therefore, it represents a potentially interesting system for applications where both conducting and luminescent properties are required.

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Conclusion

A monolayer of 5,10,15,20-tetrakis(hydroxyphenyl)-porphyrin molecules covalently assembled on a Si (100) surface, functionalized by 10-undecylenic acid, was synthesized. The monolayer was characterized by monochromated angle resolved X-ray photoelectron spectra and atomic force microscopy measurements. XPS O 1s, C 1s, and N 1s spectra show evidence of covalent linkage of porphyrin molecules to the functionalized substrate surface. AFM images and lithography support a Si(100)-supported 10-undecylenic acid porphyrin monolayer with a plausible indication that porphyrin molecules bind the surface in a vertical fashion. In addition, the system shows a promising luminescent behavior, which is potentially interesting for fabrication of molecular-based information storage materials and, in general, for high-quality sensor devices where both conducting and luminescent properties are required.

Acknowledgment. The authors thank the NATO (SfP project 981964) and the Ministero Università e Ricerca (MUR, Roma) for financial support (PRIN 2005 and FIRB 2003). Prof. S. Giuffrida is fully acknowledged for PL measurements.

CM071450U