# Redox-active Si(100) surfaces covalently functionalised with [60]fullerene conjugates: new hybrid materials for molecular-based devices<sup>†</sup>‡

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Herein, we report the covalent immobilisation, through Si–C bonds, of various [60]fullerene derivatives on flat silicon surfaces following three different preparative protocols. Each synthetic strategy comprises a two-step approach that includes a pre-modification step of the Si(100) surface with an organic monolayer bearing a terminal functionality that undergoes a bond-forming reaction with a [60]fullerene synthon as characterized by X-ray photoelectron spectroscopy (XPS) measurements. Water contact angle measurements clearly showed a characteristic change of the surface hydrophobicity upon covalent immobilisation of the carbon functions. The hybrid [**4b**-Si(100)] surfaces, containing [60]fullerene-ferrocene fragments, were also investigated by means of cyclic voltammetry (CV), and were revealed to be exceptionally robust towards repeated reduction–oxidation cycles. Moreover, several surface-confined redox couples were observed in CH<sub>3</sub>CN solution. The surface coverage was measured to be *ca.*  $2.5 \times 10^{-11}$  mol cm<sup>-2</sup>.

# Introduction

The integration of circuits (wires, resistors, capacitors, and transistors) on silicon substrates was the essential stimulus for the increase of computational power in the late 1960s. By developing new techniques to fabricate smaller and smaller components, scientists have enormously increased the speed and capabilities of computing.1 According to "Moore's Law", the technological advancement should reduce the components to the molecular scale in 20 years.<sup>1-3</sup> Even considering further technological progress in the manufacturing of integrated circuits, both materials (such as Si) and processes currently in use will reach their fundamental limits some time in the future.<sup>1,3</sup> Based on such considerations, many scientists started to focus their attention on the development of hybrid electronic devices in which surfaces are modified with single molecules or molecular assemblies.<sup>2,4</sup> Common electronic devices, such as diodes, are essentially controlled by the electronic properties of their interfaces and any changes of the chemical and electronic properties between

the surface and the bulk have great importance.<sup>5,6</sup> Therefore, controlling the electronic properties of semiconductor surfaces is indispensable for constructing devices and for fine-tuning their performance.5,7,8 Among all possible surface treatments, chemical modification with organic molecules9 provides a promising tool for the modulation of the superficial electronic properties.<sup>10</sup> About 10 years ago, scientists started to study how to chemically functionalise porous<sup>11</sup> and flat<sup>12</sup> silicon surfaces by introducing covalent Si-C bonds.13 Beside the improvement of the chemical and physical stability of such surfaces,14,15 the covalent modification allowed chemists to remotely tune the superficial physical properties of silicon by immobilising versatile functional organic molecules the properties of which could be exploited toward the engineering of advanced hybrid materials for sensor,16 electronic,<sup>8,17-19</sup> magnetic,<sup>20</sup> memory storage devices<sup>21</sup> and biological<sup>22,23</sup> applications. Several functionalisation methodologies have been thus developed to modify free-oxide silicon substrates via thermal hydrosilylation,15 photochemical (UV or visible) irradiation,24 electrochemical reduction,25 acid- and metal-catalysed hydrosilylation.26 The choice of the methodology to form Si-C bonds strictly depends on the stability and chemical structure of the attached functional groups. For instance, different electronical active groups such as ferrocene27 and porphyrins19,28 could be immobilised on silicon surfaces, showing very promising potential properties as molecular-based charge-storage devices.

For its part, [60]fullerene is one of the most widely used electron acceptor components in molecular dyads and many efforts have been focused on the development of hybrid materials containing  $C_{60}$  and its derivatives with the aim to study their electron transfer properties.<sup>29,30</sup> Surface modification utilising [60]fullerene modules is currently of high importance, owing to the possibility of transferring the unique electronic [60]fullerene properties to bulk materials by surface coating.<sup>29,31</sup> For instance, this type of organic layer containing redox centers at a fixed distance from

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a surface instead of freely diffusing, represents an important class of hybrid materials due to their potential technological applications ranging from medicinal chemistry to advanced nanostructured devices for electronic applications.<sup>31</sup> A large variety of [60]fullerene-containing self-assembled monolayers formed upon spontaneous adsorption of molecules on Au,32-34 Ag,35 Hg36 and silicon oxide37-39 surfaces have been described in the literature. In an earlier work, Cahen and co-workers have also investigated the immobilisation of [60]fullerenes derivatives on various semiconducting surfaces.40 Specifically, it has been observed that a series of [60]fullerene-derived carboxylic acids could be easily adsorbed on (n- and p-type) GaAs and ZnO crystals, revealing a strong influence of the electron-accepting [60]fullerene moieties on the superficial properties (work function and band bending) of the semiconductor as a consequence of the interaction between the frontier orbitals of the carbon spheres with the valence and conduction bands.40 To the best of our knowledge, if two works on porous silicon substrates<sup>41</sup> and one on Si(111) are excluded,<sup>42</sup> only Feng and Miller have described in 1999 the functionalisation of hydrogenated flat Si(100) with [60]fullerenes.43 In particular, they reported the self-assembly of C<sub>60</sub> molecules on flat Si(100) surfaces via direct tethering of the carbon sphere to the surface as shown by electrochemical and fast atom bombardment mass spectrometry measurements. All [60]fullerene-containing materials were found to be very stable in both acidic aqueous and polar non-aqueous solvents.43

In this paper, we thus report our synthetic strategies (Scheme 1) towards the covalent functionalisation, through Si–C bonds, of hydrogenated flat Si(100) surfaces with various [60]fullerene derivatives (*e.g.*, **4a–c**). Specifically, three strategies, each comprising a two-step approach including a pre-modification step (Step A) of the silicon surface with an organic monolayer bearing a terminal functionality that undergoes a bond-forming reaction (Step B) with pristine  $C_{60}$  or with its derivatives, have been pursued (Scheme 1). Full surface characterization with XPS and water contact angle measurements showed that all methodologies led to the immobilisation of the [60]fullerene moiety on the surface. Additionally, comprehensive electrochemical investigations on materials composed of [**4b**-Si(100)] showed the formation of redox-active and very robust hybrid materials.

# Experimental

#### Synthesis of [60]fullerene derivatives 4a-c

NMR spectra were obtained on a Jeol JNM-EX400 (400 MHz <sup>1</sup>H-NMR) and on a Varian Gemini 200 (50 MHz <sup>13</sup>C-NMR). Chemical shifts are reported in ppm using the solvent residual signal as an internal reference (CDCl<sub>3</sub>:  $\delta_{\rm H} = 7.26$  ppm,  $\delta_{\rm C} = 77.16$  ppm). The resonance multiplicity is described as s (singlet), d (doublet), dt (doublet of triplets), m (multiplet), br (broad signal). IR spectra (KBr) were recorded on a Perkin Elmer 2000 spectrometer. Electrospray ionisation (ESI) mass spectrometry measurements were performed on a Perkin-Elmer API1 at 5600 eV at University of Trieste. 4-Dimethylaminobenzal-dehyde **2a** and ferrocene carboxaldehyde **2b** were purchased from CarloErba and Aldrich respectively, and used as received. Formyl-substituted porphyrin **2c**<sup>44</sup> and *N*-Boc-protected amino-acid **1**<sup>45</sup> were prepared according to literature methods.

General synthetic procedures (Scheme 2). Synthesis of [60]fullerene conjugates 3a–c. To an oven-dried 200 mL round-bottomed flask charged with a toluene solution of  $C_{60}$  (0.52 mmol in 130 mL) and amino acid 1 (0.26 mmol), the appropriate aldehyde derivative (2a–c, 1.04 mmol) was added. After 0.5 h of sonication and 1 h of reflux under vigorous stirring, the solution was concentrated under reduced pressure, the crude purified by flash chromatography (SiO<sub>2</sub>; toluene) and the solvent evaporated in *vacuo*. Precipitation of the chromatographic fraction from CHCl<sub>3</sub> upon addition of MeOH afforded the desired fulleropyrrolidine (3a–c) as brown powder. For the spectroscopic characteristics see ESI.‡

Synthesis of [60]fullerene conjugates 4a–c: general procedure for the acidic cleavage of the *tert*-butoxycarbonyl (Boc) protecting group. To a stirred solution of the appropriate Boc-protected [60]fullerene conjugate (**3a–c**) (0.14 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL, 62.4 mmol), TFA (2 mL, 26.9 mmol) was added dropwise at 0 °C. After stirring for 16 h at 25 °C, hexane (20 mL) was added to the mixture. The suspension was filtered and the precipitate washed with methanol, hexane, toluene, and CH<sub>2</sub>Cl<sub>2</sub> until the supernatant was clear. Subsequent drying under high vacuum yielded the desired [60]fullerene-amine derivative (**4a–c**) as brown powder. In order to prevent extensive decomposition of the amine [60]fullerene precursor **4a–c**, the deprotection reaction was performed each time prior to the surface functionalisation step.

#### Functionalisation of Si(100) substrates

40% HF(aq) solution was purchased from Fluka and used as received. 11-Bromo-1-undecene, 10-undecylenic acid, 10-undecylaldehyde, NaN<sub>3</sub>, pyridine, anhydrous N,N-dimethylformamide (DMF), CH<sub>2</sub>Cl<sub>2</sub> and MeOH were purchased from Aldrich and also used as received. All chemical functionalisations of the hydrogenated silicon samples [H-Si(100)] were carried out in a  $N_2(g)$ -purged dry-box (Braun) or using standard preparative Schlenk-line procedures. The silicon surfaces used in these experiments were single crystals, polished 525  $\pm$  25  $\mu$ m thick Si(100) wafers, boron- (p-type) or phosphorus-doped (n-type), with 7–21  $\Omega$  cm resistivity (Si-Mat). Before use, the Si(100) wafers  $(1 \times 1 \text{ cm})$  were first cleaned in boiling 1,1,2-trichlorethane for 10 min and then sonicated for 5 min in MeOH at room temperature. Subsequently the samples were chemically oxidised in H<sub>2</sub>O<sub>2</sub>-HCl-H<sub>2</sub>O (2:1:8) at 353 K for 15 min, copiously rinsed with de-ionised water, chemically etched with 10% aqueous HF for 10 min and again rinsed with de-ionized water. The samples were then dried under a N2 stream and consequently covered (in a dry-box) with 11-bromo-1-undecene, 10-undecylenic acid or 10-undecylaldehyde and subjected to a 35 mW cm<sup>-2</sup> visible irradiation (quartz-iodine lamp) for 12 h. After functionalisation, the samples ([Br-Si(100)], [HO<sub>2</sub>C-Si(100)] and [HOC-Si(100)]) were subjected to three sonication cycles, 5 min each, with CH<sub>2</sub>Cl<sub>2</sub> and MeOH and then dried under a N<sub>2</sub> stream.

Amidation reaction between [HO<sub>2</sub>C-Si(100)] and the [60]fullerene conjugates (Scheme 1, path a). The surface derivatisation with [60]fullerenes was performed immersing the semiconductor [HO<sub>2</sub>C-Si(100)] substrate into a  $10 \times 10^{-3}$  M solution of EDC



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Scheme 1 The three strategies employed to covalently modify the Si(100) surfaces: Step A: Si(100) surfaces functionalisation with  $\alpha, \omega$ -bifunctional alkyl chain molecules; Step B: [60]fullerene derivatisation of the passivated Si(100) surfaces.  $h\nu$  = Visible irradiation from a quartz-iodine lamp; TFA: trifluoroacetic acid; DMF: *N*,*N*-dimethylformamide; HOBt: 1-hydroxybenzotriazole•H<sub>2</sub>O; EDC: 1-ethyl-3-(3-dimethylaminopropyl)carbodii-mide; **5** = *N*-methyl-3,4-fulleropyrrolidine fragment. **4i** = **4a**, **4b**, or **4c**.

and HOBT in dry pyridine for 15 min, followed by the addition of a  $10 \times 10^{-3}$  M solution of the selected [60]fullerene derivative (**4a–c**) in dry pyridine. After the reaction was completed (reaction time: about 48 h), the samples were removed from the reaction solution, copiously rinsed with dry pyridine, sonicated three times (5 min each) with a CH<sub>2</sub>Cl<sub>2</sub>–TFA (1 : 1) mixture, washed with MeOH and then dried under a of N<sub>2</sub> stream. The samples were stored under vacuum (10<sup>-2</sup> Torr).

1,3-Dipolar reaction between [HOC-Si(100)] and  $C_{60}$  (Scheme 1, path b). The [HOC-Si(100)] surface were immersed in a toluene

solution of  $C_{60}$  (20 × 10<sup>-3</sup> M) and sarcosine (5 × 10<sup>-3</sup> M) at reflux for 16 h. After the reaction was completed, the ([5-Si(100)]) samples were removed from solution, copiously rinsed with toluene, sonicated three times (5 min each) with toluene, CH<sub>2</sub>Cl<sub>2</sub>/TFA, MeOH and then dried under a N<sub>2</sub> stream.

1,3-Dipolar reaction between [N<sub>3</sub>-Si(100)] and C<sub>60</sub> (Scheme 1, path c). The nucleophilic substitution of the bromine-terminated Si(100) surfaces (Scheme 2) was performed using standard preparative Schlenk-line procedures.<sup>46</sup> The [Br-Si(100)] substrates were immersed in a  $10 \times 10^{-3}$  M solution of NaN<sub>3</sub> in dry DMF



Scheme 2 Synthesis of [60]fullerene derivatives 4a-c.

for 72 h. After the reaction was completed, the samples ([N<sub>3</sub>-Si(100)]) were removed from solution, copiously rinsed with dry DMF, sonicated three times (5 min each) with DMF, CH<sub>2</sub>Cl<sub>2</sub>, MeOH and then dried under a stream of N<sub>2</sub>. The 1,3-dipolar reaction with C<sub>60</sub> was performed immediately after the azide treatment. The [N<sub>3</sub>-Si(100)] surfaces were immersed in a 10 × 10<sup>-3</sup> M solution of C<sub>60</sub> in dry toluene at reflux for 16 h. After the reaction was completed, the ([C<sub>60</sub>N-Si(100)]) samples were removed from the reacting solution, copiously rinsed with toluene, sonicated three times (5 min each) with toluene, CH<sub>2</sub>Cl<sub>2</sub>-TFA (1 : 1), MeOH and then dried under a N<sub>2</sub> stream.

#### **Contact angle measurements**

The advancing contact angle of water was determined on sessile drops with a Ramé-Hart Model Automated Contact Angle Goniometer at 25 °C under atmospheric conditions. The advancing contact angle,  $\theta_a$  (H<sub>2</sub>O), was obtained by RHI 2001 imaging software at both sides of a forming 5 µL drop of water on the surface. The reported values are the average of 5–15 measurements (5 measurements in 3 different positions of the same samples recorded every 15 s).

#### X-Ray photoelectron spectroscopy

XPS results were obtained on an experimental apparatus in UHV consisting of a modified Omicron NanoTechnology MXPS system, with an XPS chamber equipped with a monochromatic X-ray source (Omicron XM-1000) and an Omicron EA-127 energy analyzer. Samples were transferred between the various experimental areas by means of linear magnetic transfer rods or manipulators. All measurements were conducted in the least possible time after sample preparation with p-type silicon substrates. Samples were produced and mounted on sample holders in a dry-box, transferred under  $N_2$  from the dry-box to the XPS facility and introduced into the XPS chamber after about 1 min air exposure. No sizeable sign of sample degradation under extended acquisition times under the X-rays was observed. The experimental conditions adopted were: excitation by Al K $\alpha$  photons ( $h\nu = 1486.7 \text{ eV}$ ), generated operating the anode at 14–15 kV, 10–20 mA. No charging was experienced by the hybrid species, as can be inferred from the Si 2p peak position, coincident with literature reports which assign a value of 99.7 eV to the Si 2p<sub>3/2</sub> bulk component. XPS atomic ratios for the functionalised hybrids were estimated from experimentally determined area ratios of the relevant core lines, corrected for the corresponding theoretical atomic cross-sections and for a square root dependence of the photoelectrons kinetic energies. The effects on quantitative analysis possibly of photoelectron diffraction at preferential directions of electron collection were minimised by mounting the Si(100) wafers always with the same orientation with respect to the analyzer axis.<sup>47</sup>

#### Electrochemistry

After monolayer formation ohmic contact was made to the back of the derivatised [4b-Si(100)] samples scratching the Si surface, rubbing it with Ga-In eutectic and attaching it to a copper contact. The electrode set-up was obtained by pressing the Si crystal against an O-ring sealing a small aperture in the PTFE cell defining an electrode area of 0.3 cm<sup>2</sup>. The electrochemical properties of the hybrid [4b-Si(100)] surfaces were explored by CV measurements in 0.1 M Et<sub>4</sub>NClO<sub>4</sub> in dry CH<sub>3</sub>CN. The electrolyte solution deliberately contained no added electroactive species. All electrochemical measurements were performed inside a dry box with a three-electrode cell, using an Autolab Electrochemical Analyzer (model PGSTAT 12, Eco Chemie BV, The Netherlands). The counter electrode was a platinum coil wire, and a silver wire immersed in a 0.01 M AgNO<sub>3</sub>-0.1 M Et<sub>4</sub>NClO<sub>4</sub> solution in CH<sub>3</sub>CN, separated from the main solution by a porous fritted glass + agar plug, served as a reference electrode. All potentials reported will be henceforth referred to this reference. The kinetic analysis was performed after correcting the cyclic voltammograms for IR drop.

### **Results and discussion**

# Strategy, preparation, and functionalisation of the Si(100) surfaces

The criteria for the design and preparation of the C<sub>60</sub>-based adsorbates are mainly related to the development of new synthetic methodologies to easily prepare modified silicon surfaces bearing redox active molecules that can be in principle used as functional hybrid materials to engineer molecular-based devices. For these applications, [60]fullerene layers should possess electronic transducing properties together with a high chemical and structural stability. In principle, there are two popular approaches to anchor [60] fullerenes onto surfaces: covalent (via functionalisation of  $C_{60}$ with suitable groups that undergo a chemisorption on the surface or via pre-modification of the surface by adsorption of an organic monolayer bearing a terminal functionality that undergoes a bond-forming reaction with C<sub>60</sub> or its derivatives) or non-covalent (pre-adsorption on the surface of an organic layer which assembles with pristine C60 or its derivatives through a non-covalent molecular recognition approach).<sup>31</sup> As shown in Scheme 1, our strategies involved the functionalisation of a silicon surface with [60]fullerene derivatives that exposes their carbon spheres at the aliphatic  $\omega$ -terminus to the outer surface. Since the linker attached to the [60]fullerene moiety could have a large influence on the electrochemical stability of the layer, we have decided to explore the versatility of these synthetic strategies towards different reactions leading to different linkers. Therefore, based on the above-described requirements, the functionalisation strategies reported in Scheme 1, in which the [60]fullerene moieties (Step B) are immobilised to a pre-adsorbed layer (Step A) having terminal functionalities which undergo bond-forming reactions (Scheme 1, paths b and c) with C<sub>60</sub> (leading to aza[60]fullerene and [60]fulleropyrrolidine derivatives for [C<sub>60</sub>N-Si(100)] and [5-Si(100)], respectively) or its derivatives (4a-c, via an amidic bond for [4a-Si(100)], [4b-Si(100)] and [4c-Si(100)], Scheme 1 path a) were chosen for the covalent attachment of the [60]fullerene moiety.

[60]Fullerene dyads **3a–c** were easily prepared through the 1,3dipolar cycloaddition of azomethine ylides (formed in situ starting from the corresponding aldehyde (2a-c) in the presence of amino acid 1) to C<sub>60</sub> (Scheme 2).48 All compounds were fully characterised by the standard spectroscopic and analytical techniques, giving satisfactory results. In particular, the structures of all [60]fullerene-containing dyads 3a-c were assessed by ESI mass spectrometry, 1H- and 13C-NMR, UV-VIS, and IR spectroscopy. The broadening of the proton signals in the NMR spectra can be attributed to the restricted rotation at 298 K suffered by the phenyl (molecules 3a and 3c) and the cyclopentadienyl groups at the  $\alpha$ -position of the fulleropyrrolidine ring.<sup>49</sup> Fulleropyrrolidine amine-bearing precursors 4a-c were prepared by acidic cleavage of the tert-butoxycarbonyl (Boc) protecting group in the presence of TFA following standard synthetic protocols.45 Compound 4c was further remetallated with a saturated solution of  $Zn(OAc)_2$  in MeOH.

Given the sensitivity of the monolayer structure towards various external parameters (reaction conditions and substrate) and the different types of averaging associated with various spectroscopic techniques, the use of several complementary methods is necessary in order to obtain a complete chemical and structural description of the prepared organic thin films.<sup>30</sup> Therefore, XPS and water contact angle measurements were conducted with the aim of studying and confirming the covalent modification of the silicon surfaces.

#### X-Ray photoelectron spectroscopy

XP spectra were taken in order to both assess the nature of the substrate-molecule interaction and monitor the progressive build-up of the final hybrid system along the different functionalisation steps depicted in Scheme 1. This section is organised as follows: we first compare the results from the preparation protocols of Si(100) surfaces functionalised with 10-undecylenic acid, 10-undecylaldehyde, and the azide terminus (Step A). The results of curve-fitting analysis allow identification of the peculiar features of each terminating functional group. Then we examine the spectral evolution related to the establishment of a bond between the C<sub>60</sub> or its derivatives and the  $\alpha, \omega$ -bifunctional alkyl molecules immobilised on the surface (Step B). Each relevant photoemission region (Si 2p, C 1s, N 1s and Fe 2p) is presented separately, and its relevance to the overall assignment of the characteristic nature and electronic structure of the single species discussed.

Si 2p photoelectron line. Step (a)—Si(100) surfaces passivated with  $\alpha,\omega$ -bifunctional alkyl chain molecules. The Si 2p regions are displayed after passivation of the [H-Si(100)] surfaces with  $\alpha,\omega$ -bifunctional alkyl chain molecules, resulting in azide-, aldehyde-, and carboxylic-terminated surfaces ([N<sub>3</sub>-Si(100)], [HOC-Si(100)], and [HO<sub>2</sub>C-Si(100)]), respectively, shown in Fig. 1, spectra (a).

Two resolved spin-orbit split components result from curvefitting (not shown here), which are respectively related to the contribution from bulk Si atoms, located at a binding energy (BE) of 99.7 eV, and to a surface component, positively shifted by 0.35 eV, i.e., falling in the region of Si-C and Si-H bonds. The depth of the valley between the two spin-orbit components (trough depth) is closely comparable between the different terminated surfaces, as expected from the presence of Si-C bonds to an equal extent. A flat line results in the energy region typical for silica (103-104 eV), for both [HOC-Si(100)] and [HO<sub>2</sub>C-Si(100)] surfaces, hinting at an oxide-free functionalised surface. For the [N<sub>3</sub>-Si(100)] surfaces a modest SiO<sub>2</sub> signal could be detected, probably originating from the Si sites reacting with residual traces of O<sub>2</sub> and H<sub>2</sub>O still present during the preparation of the samples in the Schlenk line. This step was necessary for the substitution of the Br termination with the azide reactive group.46 A quantification of the SiO2 amount was performed applying a conventional attenuation model for ultrathin layers of SiO<sub>2</sub> grown on Si substrates based on the relative intensity ratio between bulk and silica-related Si 2p peak components. The results are reported in Table 1, where a value of 0.57 nm is associated to the [N<sub>3</sub>-Si(100)] surface. Notably, no SiO<sub>2</sub> has been observed for the Br-, HOOC-, and OHC-terminated surfaces (see Table 1). The low values of SiO<sub>2</sub> thickness suggests a fractional coverage of the surface by the oxide (as further confirmed by electrochemical characterization, vide infra) and



Fig. 1 XPS spectra taken in the Si 2p region. Top: (a)  $[HO_2C-Si(100)]$  and (b) [4b-Si(100)]. Middle: (a) [HOC-Si(100)] and (b) [5-Si(100)]. Bottom: (a)  $[N_3-Si(100)]$  and (b)  $[C_{60}N-Si(100)]$ .

should be taken as an indication of the relative soft impact of the preparation procedures on the final surfaces.

**Step (b)**—[60]Fullerene derivatisation of the modified Si(100) surfaces. Upon reaction of the [HOC-Si(100)] and [HO<sub>2</sub>C-Si(100)] surfaces with C<sub>60</sub> and its conjugates **4a–c**, respectively, a slight increase of the signal in the region of silica was observed for both materials, while for the [N<sub>3</sub>-Si(100)] surfaces the SiO<sub>2</sub> thickness remained comparable (see curves (b) in Fig. 1). Quantification of the Si oxide thicknesses (Table 1) revealed values of 0.74, 0.76, 0.47, and 0.48 nm for the [**4b**-Si(100)], [**4c**-Si(100)] (not shown here), [**5**-Si(100)] and [C<sub>60</sub>N-Si(100)] surfaces, respectively. Such values still allow electrical communication between the Si bulk and the anchored redox species.

**C** 1s photoelectron line. Step (a)—Si(100) surfaces passivated with  $\alpha, \omega$ -bifunctional alkyl molecules. The C 1s region for the [N<sub>3</sub>-Si(100)], [HOC-Si(100)], and [HO<sub>2</sub>C-Si(100)] surfaces are displayed in Fig. 2–4, insets (a). Three different components are visible for the [N<sub>3</sub>-Si(100)] sample. The higher peak at 285.4 eV is assigned to carbon atoms of the alkyl chain, while minor components shifted by -0.6 and +1.6 eV are related to C–Si and C–N terminal ends of the aliphatic chains. Both features are in a 1:9 area ratio with the central peak, as expected from the molecular stoichiometry when the N<sub>3</sub>– end-group



**Fig. 2** XPS spectra taken for (a)  $[N_3$ -Si(100)] and (b)  $[C_{60}$ N-Si(100)] surfaces in the C 1s region.



Fig. 3 XPS spectra taken for (a) [HOC-Si(100)] and (b) [5-Si(100)] surfaces in the C 1s region.

remains unchanged. For the [HOC-Si(100)] surfaces, four components were found by curve-fitting procedure, the higher being related to methylene groups of the aliphatic chains, as in the previous case. The minor components, shifted by -0.5, +0.6, +1.3 eV with respect to the higher peak, are respectively

Table 1 SiO<sub>2</sub> thickness as determined by XPS measurements

	[Br-Si(100)]	[HO <sub>2</sub> C-Si(100)]	[ <b>4b-Si</b> (100)]	[ <b>4c</b> -Si(100)]	[HOC-Si(100)]	[5-Si(100)]	[N <sub>3</sub> -Si(100)]	[C <sub>60</sub> N-Si(100)]
d <sub>ox</sub> /nm	Not detected	Not detected	0.74	0.76	Not detected	0.47	0.57	0.48



Fig. 4 XPS spectra taken for (a)  $[HO_2C-Si(100)]$  and (b) [4b-Si(100)] surfaces in the C 1s region.

attributed to C-Si, C(-CHO) and C(=O)H carbon atoms. Each of them is in a stoichiometric 1:8 area ratio with the alkylcentred peak, hinting at a covalent attachment to the Si(100) surface through the reaction with the olefinic extremity. Four different components in the same relative ratios were also found for the [HO<sub>2</sub>C-Si(100)] surfaces, the higher, centred at 285.7 eV, being related to the aliphatic chains of the molecules. The major difference with the previous case is the presence of a high-BE component (290.2 eV) that can be assigned to the C(=O)OH ending group, accompanied by its  $\alpha$ -C at 287.4 eV. These results again support our hypothesis that the terminal alkene group underwent covalent reaction with the Si surface. Step (b)-[60]Fullerene functionalisation of the passivated Si(100) surfaces. The C 1s spectra of the hybrid surfaces ([C<sub>60</sub>N-Si(100)], [5-Si(100)] and [4b-Si(100)]) resulting from the reaction with  $C_{60}$ or its derivatives are shown in Fig. 2-4 (insets b). In all cases, the C atoms of the fullerene cage predominantly contribute to the peak at 285.3 eV,<sup>33</sup> accompanied by a minor peak at 285.6 eV (alkyl chain). The former feature can be reproduced with a Gaussian-Lorentzian mixed lineshape slightly exponentially asymmetric towards high BEs.33,50 Two shake-up resonances of low intensity shifted by +3.5 and +6.0 eV from the parent peak are associated with the carbon cage atoms.<sup>33,51</sup> The contribution

from C–N bonds are found at +1.7 eV with respect to the  $C_{60}$ -cage atoms.<sup>33,52</sup> XPS quantification for the three hybrids yields peak intensities for the C–N and the chain C atoms in the right stoichiometric ratio with respect to the carbons of the fullerene moiety, supporting the proposed elemental composition of the hybrid materials (Table 2).

**N 1s photoelectron line.** Fig. 5 (see also Table 3) shows the N 1s region for the  $[N_3$ -Si(100)] and [60]fullerene-terminated surfaces ([**4b**-Si(100)], [**5**-Si(100)] and  $[C_{60}N$ -Si(100)]). The  $[N_3$ -Si(100)] substrate shows two peaks [curve (a)] at 401.6 and 405.4 eV, with a 2 : 1 peak area ratio. The high- and low-BE peaks are respectively assigned to the central, electron-deficient, N atom of the N<sub>3</sub> group and to the two nearly equivalent azide N atoms.<sup>46,53</sup> After reaction with C<sub>60</sub> (curve (b)), the high-BE peak disappears and a single component is found in the classical energy range of tertiary aliphatic amines at 400.5 eV.<sup>52</sup> This is in agreement with the presence of aza[60]fullerene derivatives on the surface as formed from the 1,3-dipolar cycloaddition reaction of the N<sub>3</sub> terminal group with C<sub>60</sub> followed by the loss of N<sub>2</sub>. The same BE value of 400.5 eV is found for the N 1s peak of [**5**-Si(100)] surfaces, where a tertiary aminic group is supposed



Fig. 5 XPS spectra taken in the N ls region. Top: [4b-Si(100)]. Middle: [5-Si(100)]. Bottom: (a)  $[N_3$ -Si(100)] and (b)  $[C_{60}N$ -Si(100)].

Table 2 XPS BE (eV)/FWHM (eV) data characterizing the C 1s photoelectron line

C 1s	[HO <sub>2</sub> C-Si(100)]	[ <b>4b-</b> Si(100)]	[HOC-Si(100)]	[ <b>5</b> -Si(100)]	[N <sub>3</sub> -Si(100)]	[C <sub>60</sub> N-Si(100)]
C–Si	284.6/1.4		284.9/1.1		284.8/1.2	
C=C		285.4/1.3		285.3/1.3		285.3/1.2
C–C	285.7/1.4	285.6/1.3	285.4/1.1	285.6/1.3	285.4/1.2	285.6/1.2
C–N		287.1/1.5		287.0/1.2	287.0/1.2	287.0/1.3
C-COOH	287.4/1.4					
COOH	290.2/1.4					
C–CHO			286.0/1.1			
CHO			286.7/1.1			

N 1s	[ <b>4b</b> -Si(100)]	[ <b>5</b> -Si(100)]	[ <b>4c</b> -Si(100)]	[N <sub>3</sub> -Si(100)]	[C <sub>60</sub> N-Si(100)]
$NR_3 \\ -N=N^+=N^- \\ -N=N^+=N^- \\ N\cdots Zn \\ [(NH)_4]^{2+}$	400.8/2.5	400.5/2.5	399.1/2.0 400.9/2.0	401.6/1.9 405.4/1.9	400.5/2.8

Table 3 XPS BE (eV)/FWHM (eV) data characterizing the N 1s photoelectron line.



Fig. 6 XPS spectrum taken for [4c-Si(100)] in the N 1s region.

to form upon the 1,3-dipolar cycloaddition reaction with  $C_{60}$ .<sup>52</sup> A small positive N 1s BE shift found in the case of [**4b**-Si(100)] is compatible with the additional presence of a N atom employed in an amidic linkage.<sup>52</sup>

The N 1s spectrum of [4c-Si(100)] is shown in Fig. 6. A free base porphyrin has two symmetry-distinct and electronically non-equivalent N atoms. As widely described in the literature, these non-equivalent atoms are related to the unprotonated and protonated porphyrinic N atoms.<sup>54</sup> We have inferred from previous XPS studies on various porphyrins that these two N atoms present a constant BE separation from the macrocycle C 1s of 113 and 115 eV, respectively, with a small associated uncertainty. Once the free-base porphyrin is complexed, the two components converge into a single peak, i.e., four equivalent metal-ligated N atoms, and the energy separation from C 1s becomes 114  $\pm$  0.3 eV. Such a parameterised analysis allows for direct comparison among different porphyrins, both before and after anchoring, largely compensating for the electronic effects of specific substituents attached to the porphyrin ring, which can shift sizeably its BE.55 In our previous reports on metalloporphyrins bound to Si(100) and Si(111) surfaces,<sup>56</sup> we found that the N 1s region can be a complex peak even for the metallated porphyrins, where at least two components result from curve fitting, apart from any low-intensity satellite line. The result is unexpected, and it lacks mention in previous reports for closely related systems.<sup>57</sup> The Zn(II)-porphyrinate moiety present in the hybrid materials investigated here shows a N 1s XP spectrum (Fig. 6) where two main components can be located at 399.1 and 400.9 eV, with an associated shift from the C 1s peak of 113.7 and 115.6 eV, respectively (see Table 3). These values allow for a straightforward assignment of the N 1s low-BE component, which support the presence of N atoms in intact porphyrinates. As already reported by us for different metallated porphyrins, the N 1s high-BE component represents a true electronic state of the tetrapyrrolic system.<sup>56</sup> As to its assignment,

one can note that the corresponding N 1s BE falls at higher values than that reported for pyrrolic nitrogens in free-base structures, and its energy separation (N 1s-C 1s) of 115.6 eV is consistent with the diacid derivative carrying a 2+ charge on the ring (in Table 3 referred to as  $[(NH)_4]^{2+}$ ) recently reported in the literature.<sup>58</sup> As to the N/Zn atomic ratio, it is worth noting that only by adding both N 1s peaks is a value of 3.8, close to the theoretical stoichiometric value of 4, obtained.<sup>56</sup> Consistently with our previous reports with porphyrins, all these results recall for a demetallation reaction occurring upon anchoring the molecule on the surface, leaving the porphyrin ring in two related portions, while the Zn(II) ions remain adsorbed on the surface (see Fig. S7 in the ESI<sup>‡</sup>). It is thought that, in the experimental conditions adopted here, acidity can be locally generated at reaction sites. The presence of protonated N atoms might thus result from the acidic *in-situ* demetallation of the Zn(II)-porphyrin complex. Finally, the low intensity peak located at 403.1 can be associated to a shake-up feature, resulting from a core-ionized valence-excited final state.59

**Fe 2p photoelectron line.** Inspection of the Fe 2p region of the [**4b-Si**(100)] sample after curve-fitting (see Fig. 7 and Table 4) reveals Fe species in both (II) and (III) oxidation states, at 708.7



Fig. 7 XPS spectrum taken for [4b-Si(100)] in the Fe 2p region.

Table 4 XPS BE (eV)/FWHM (eV) data characterizing the Fe 2p photoelectron line  $\$ 

	Fe(II) 2p <sub>3/2</sub>	Fe(III) 2p <sub>3/2</sub>	Shake-up	Fe(II) 2p <sub>1/2</sub>	Fe(III) 2p <sub>1/2</sub>
[ <b>4b-</b> Si(100)]	708.7/1.0	712.4/3.6	717.0/4.9	721.3/1.3	725.0/4.9

and 712.4 eV respectively, with Fe(III) being predominant. These values and the corresponding peak widths are consistent with our previous findings on ferrocene derivatives anchored on Si(100). The presence of Fe(III) has been invariably found for the different ferrocene derivatives explored by us after covalent attachment to Si(100).<sup>17,27,46,60</sup> The high relative Fe(III)/Fe(II) ratio found for the [**4b**-Si(100)] samples can be taken as the result of the strong intramolecular charge-transfer type interaction between the [60]fullerene and the ferrocenyl moiety. In fact, such a high Fe(III)/Fe(II) ratio for freshly prepared Si-confined ferrocene hybrids has never been detected under these conditions by us, but only invariably observed after extensive and prolonged redox cycling.<sup>27</sup>

#### Surface wettability

The [60]fullerene-containing surfaces were also characterised by wetting contact angle (defined also as water contact angle or contact angle of wettability) measurements, and the results are reported in Table 5. The main information that can be extrapolated from such an experiment is the hydrophobicity (as a consequence of the presence of a lipophilic organic thin film) of the surface by measurement of the contact angle ( $\theta_a$ ) formed between a drop of water and the coated surface. The experimental contact angle of wettability on [H-Si(100)] ( $80 \pm 2^{\circ}$ ) is higher than that of non-etched (prior to HF treatment) Si(100) surfaces  $(10 \pm 2^{\circ})$ , indicating the higher hydrophilicity of the latter because of the presence of the SiO<sub>2</sub> layer. After the linkage of the [60]fullerene moieties, the water contact angle significantly change to  $66 \pm 4^{\circ}$ ,  $70 \pm 3^{\circ}$ ,  $78 \pm 2^{\circ}$ ,  $81 \pm 1^{\circ}$  and  $100.9 \pm 0.3^{\circ}$ for [5-Si(100)], [C<sub>60</sub>N-Si(100)], [4a-Si(100)], [4b-Si(100)] and [4c-Si(100)], respectively (Table 5), suggesting the presence of the carbon-based hydrophobic layer that is consistent with our structural model in which the all-carbon moieties are exposed at the solid/air interface. The difference in the wettability properties between the  $[C_{60}N-Si(100)]$  and [5-Si(100)] surfaces can be ascribed to the different organisations of the carbon spheres with respect to the external surface as a consequence of the different linking groups (the aziridine-like and the pyrrolidine ring for [C<sub>60</sub>N-Si(100)] and [5-Si(100)], respectively), while the discrepancies between the [4a-Si(100)], [4b-Si(100)] and [4c-Si(100)] surfaces are mainly attributed to the different hydrophobicities (N, N'-dimethylanilinyl < ferrocenyl < porphyrinyl) of the R groups, which are also externally exposed at the solid/ air interface. These contact angles closely correspond to the values reported in the literature for thin films of [60]fullerenes confined on Au,<sup>23,32</sup> Hg,<sup>36</sup> GaAs,<sup>40</sup> ITO,<sup>37</sup> Si(111),<sup>43</sup> and silicon oxides.<sup>38</sup>

#### Electrochemical measurements

The representative electrochemical studies of the hybrid surfaces were essentially performed on the hybrid [4b-Si(100)] samples in a dry 0.1 M solution of  $Et_4NClO_4$  in  $CH_3CN$ . In a typical cyclic

voltammogram of molecule 3b in solution (see Fig. S8 in ESI<sup>‡</sup>), three electrochemically, [60]fullerene-centred, reversible waves are observed, and the redox potentials for the first, second and third one-electron electrochemical processes are -0.93, -1.34 and -1.94 V, respectively. In addition, in the anodic scan, a reversible redox wave centred at 0.22 V corresponding to the Fc/Fc<sup>+</sup> couple is also shown. Fig. 8 shows a typical CV trace of a p-doped [4b-Si(100)] substrate in the cathodic region under illumination conditions. Two partially reversible CV waves are observed, and the redox potentials for the first and second one-electron reductions are -0.80 and -1.18 V, respectively. It is very likely that these peaks clearly resemble those centred on the [60]fullerene moiety as has been shown for other [60]fullerenecontaining SAMs.<sup>61</sup> The potential for the first [60]fullerenecentred reduction of [4b-Si(100)] substrate is positively shifted by 13 mV compared to that measured in solution.

Fig. 9 shows a typical CV of a [4b-Si(100)] substrate in the anodic region. An electrochemically reversible one-electron



Fig. 8 Cyclic voltammogram of [4b-Si(100)] in CH<sub>3</sub>CN (+0.1 M Et<sub>4</sub>N-ClO<sub>4</sub>). Scan rate:  $1 \text{ V s}^{-1}$ .



Fig. 9 Cyclic voltammogram of [4b-Si(100)] in CH<sub>3</sub>CN (+0.1 M Et<sub>4</sub>N-ClO<sub>4</sub>). Scan rate:  $1 \text{ V s}^{-1}$ .

Table 5 Advancing contact angles ( $\theta a$ ) of water on [60]fullerene-containing Si(100) surfaces.

	[C <sub>60</sub> N-Si(100)]	[4a-Si(100)]	[ <b>4b-</b> Si(100)]	[ <b>4c</b> -Si(100)]	[5-Si(100)]	[HO <sub>2</sub> C-Si(100)]	SiO <sub>2</sub>	[H-Si(100)]
$\theta_{\rm a}$	$70 \pm 4$	$78 \pm 2$	81 ± 1	$100.9 \pm 0.3$	$66 \pm 4$	58 ± 1	$10 \pm 2$	80 ± 2

process is observed, which can be unambiguously attributed to the ferrocenvl moiety. The  $E^{\circ}$  value estimated from the mean of the anodic and cathodic peak potentials, was 225 mV vs. Ag/Ag<sup>+</sup>. In order to study the role of the charge carriers, CV measurements were performed in the dark and under light illumination (red laser light). No limiting effects were observed under illumination conditions, indicating that with such silicon substrates the electron transfer is not limited by the number of charge carriers and it can occur via the valence band. The first CV scan profile shows very symmetric Fc/Fc<sup>+</sup> ox/red peaks, with a full width at half maximum ( $\Delta E_{\rm FWHM}$ ) of about 100 mV and 9 mV of potential splitting ( $\Delta E_{pp} = E_{pa} - E_{pc}$ ) between the anodic  $(E_{\rm pa})$  and cathodic  $(E_{\rm pc})$  peak potentials. Such data are comparable to those obtained with Si(100) surfaces covalently modified following a similar photochemical reaction as that used in this work using a vinylferrocene derivative, indicating reversible behaviour of the SAM attached to the silicon surface.<sup>17</sup> Notably, no evidence for substantial repulsive interactions between neighboring ferrocenyl groups<sup>62</sup> was observed due to the relatively narrow width (< 100 mV) of the CV waves. This finding supports the model for which all molecules constituting the monolayer are very much accessible for electron transfer from and to the substrate, behaving independently within the layer.

Representative CVs for the [4b-Si(100)] surfaces in CH<sub>3</sub>CN (+0.1 M Et<sub>4</sub>NClO<sub>4</sub>) at different scan rates ranging from 0.5 to 10 V s<sup>-1</sup> are shown in Fig. 10 (top). As can be inferred from the inspection of Fig. 10 (bottom), the anodic and cathodic peak currents were found to linearly scale with the scan rate  $\nu$  rather than with  $\nu^{1/2}$ , indicating a surface-confined redox process. This trend is characteristic of a reversible (Nernstian) electrochemical process, wherein the relative activity of the Fc/Fc<sup>+</sup> couple is uniform throughout the film and at the equilibrium with each applied electrode potential. The surface coverage



**Fig. 10** Top: Cyclic voltammogram of [**4b**-Si(100)] in CH<sub>3</sub>CN (+0.1 M Et<sub>4</sub>NClO<sub>4</sub>) recorded at different potential scan rates in the range between 0.5 and 10 V s<sup>-1</sup>. Bottom: linear dependence of the anodic ( $\blacksquare$ ) and cathodic ( $\bigcirc$ ) peak currents on the potential scan rate.

estimated on the scan-rate dependence of the anodic and cathodic peak currents was found to be approximately  $2.5 \times 10^{-11}$  mol cm<sup>-2</sup>, which is lower than the theoretically and experimentally determined value of a densely organized fcc-packed monolayer of pristine  $C_{60}$  ( $1.9 \times 10^{-10}$  mol cm<sup>-2</sup>). This value was found to be similar to that ( $1.4 \times 10^{-11}$  mol cm<sup>-2</sup>) reported by Feng and Miller for their  $C_{60}$ -functionalised Si(100) surfaces.<sup>43</sup>

Repeated CV experiments showed that after 120 consecutive potential scans of the [4b-Si(100)] surface in the range between 0.0 and 0.5 V did not significantly change the shape of the CV traces (Fig. 11). These results clearly indicated that the developed protocol yields stable modified [4b-Si(100)] surfaces. Additionally, no major shifts of the oxidation peak were observed indicating that the energy and the chemical nature of the oxidation process remained unaltered. In contrast, the cathodic peak shifted to more negative potentials as the number of cycles increased, showing that the reduction process becomes energetically less favourable (Fig. 12). We tentatively attribute this effect to the tendency of ionic species such as the Fc<sup>+</sup> cations to couple with anions bound to the surface (for example such as silanol groups or surface-adsorbed negatively charged species coming



Fig. 11 Cyclic voltammograms for a [4b-Si(100)] electrode in CH<sub>3</sub>CN (+0.1 M Et<sub>4</sub>NClO<sub>4</sub>): first cycle (—) and after 120 consecutive potential scans (- - -). Scan rate:  $1 V s^{-1}$ .



Fig. 12 Dependence of the anodic  $(\bigcirc, E_{pa})$ , cathodic  $(\square, E_{pc})$ , and peak–peak separation ( $\Delta$ )  $\Delta E_{pp}$  potentials of the Fc/Fc<sup>+</sup> couple on the scan rate.



Fig. 13 Cyclic voltammograms of [4b-p-Si(100)] ( $\longrightarrow$ ) and [4b-n-Si(100)] (--) in CH<sub>3</sub>CN (+0.1 M Et<sub>4</sub>NClO<sub>4</sub>). Scan rate: 1 V s<sup>-1</sup>.

from the electrolyte), resulting in a final stabilisation of the Fc<sup>+</sup> species.

In the functionalised [4b-nSi(100)] surfaces, in contrast to what observed on [4b-pSi(100)], the electrochemically active redox processes were controlled by the photon flux (i.e., the current of the redox process is proportional to the light intensity shone on the electrode). The redox peaks were found to be shifted by ca. 0.4 V towards negative values with respect to the reference redox potentials as measured for the functionalised pSi(100) (Fig. 13). The peak current at nSi(100) surfaces (see ESI<sup>+</sup> Fig. S9) is limited by the photon flux, *i.e.* the irradiation of the sample with a low-intensity light emphasises the molecular redox behaviour over the Si(100) oxidation reaction under intense illumination conditions. This explains why such currents are lower than the peak currents measured for the p-Si surfaces (ESI<sup>+</sup> Fig. S9), due to the thermalised holes already abundant at the p-Si valence band edge in the dark. A direct comparison of the CV profiles of the two electrodes is shown in Fig. 13. The peak potentials, compared to that of the Fc/Fc<sup>+</sup> redox couple dissolved in the same supporting electrolyte and measured at a Pt wire electrode (0.08 V), indicate the occurrence of a slight negative and positive photovoltage shift with the n-Si and p-Si surfaces, respectively. From such data an overlapping of the valence band of the p-Si with the redox level of the Fc/Fc<sup>+</sup> couple of the grafted fullerene-ferrocene dyads is inferred.

# Conclusions

In summary, we have shown that different two-step synthetic methodologies can be used to covalently immobilise  $C_{60}$  and its derivatives on flat hydrogenated Si(100) surfaces. All [60]fullerene-modified surfaces were fully investigated by means of XPS spectroscopy and water contact angle measurements. In particular, CV measurements performed with the [4b-Si(100)] substrate, clearly showed the formation of exceptionally stable hybrid materials exhibiting reversible electrochemical behaviour. Although more work is needed in order to improve the technology in terms of surface coverage, the synthetic methodologies developed here could open new possibilities of preparing functionalized hybrid silicon surfaces bearing redox-active molecules capable of undergoing multi-electron transfer processes over

a desired potential range. In principle, such [60]fullerene-confined surfaces could be used as electronic components for molecularbased storage devices and for medical-/bio-applications acting as radical scavengers for the protection of cells against death.

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