Porphyrin anchoring on Si(100) using a β -pyrrolic position[†]

Hui Liu,^{*a*} Florence Duclairoir,^{**b*} Benoit Fleury,^{*b*} Lionel Dubois,^{*b*} Yves Chenavier^{*b*} and Jean-Claude Marchon^{**b*}

Received 21st January 2009, Accepted 27th February 2009 First published as an Advance Article on the web 24th March 2009 DOI: 10.1039/b901309a

Nickel(II) β -azido-*meso*-tetraphenylporphyrin was successfully anchored on silicon using a bifunctional linker that bears two terminal alkyne functions by the sequence (i) hydrosilylation of a C=C triple bond of the linker by surface Si–H groups and (ii) 1,3-Huisgen cycloaddition between the alkyne-terminated silicon surface and the azidoporphyrin derivative.

Introduction

The semiconductor industry is facing the problem of increasing costs associated with technological scaling. Efforts are currently being undertaken in order to find alternative architectures, materials, or technological processes, and molecule-based devices are considered as a promising approach. Redox-active molecules are potential candidates for memory applications. Heterostructures using metalloporphyrins grafted on indium oxide- or silicon-based devices have been shown to display intriguing memory effects.¹ Bistable molecules that are able to switch from one "0" state to another "1" state have been widely studied for molecular electronics applications.² Bridled chiroporphyrins³ that display conformational interconversion depending on the size or oxidation state of their central metal are the focus of current investigation in our group. We are exploring the possibility of using these bistable systems as discrete charge storage elements in non-volatile molecular memories, which implies their anchoring on a silicon surface as the first step.

[†] Electronic supplementary information (ESI) available: NMR and IR of compound **5**; MIR of surface **2** and **3**; global XPS of surface **2** and **3**; CV data. See DOI: 10.1039/b901309a

Although several procedures for the immobilisation of tetraphenylporphyrins (TPP) on silicon using a *para*-phenyl position have been described,^{1,4,5} none have been devised so far using a β -pyrrolic position of porphyrins. The aim of this investigation was therefore to develop a suitable protocol for silicon anchoring of those porphyrins, such as bridled chiroporphyrins, that cannot be easily functionalised on their *meso* positions but display accessible β -pyrrolic positions. In this study a NiTPP derivative was used as a model for this type of porphyrins.

In this context, we have been inspired by several reports describing a two-step grafting of molecules on silicon by "click chemistry". A procedure developed by Gooding *et al.* was thought to be fit for the immobilisation of porphyrins bearing a β -pyrrolic azido function (Fig. 1).^{6a} The envisioned sequence involves (i) nonadiyne immobilisation on the surface by hydrosilylation⁷ and (ii) 1,3-Huisgen cycloaddition⁸ reaction between the azido-porphyrin and the modified Si(100) surface. Functionalisation of silicon using this sequence would offer several considerable advantages. The functions involved have very specific XPS and FT-IR signatures, allowing easy monitoring of the reaction.^{9,10} Moreover, a long alkyl linker would promote the formation of a dense monolayer protecting the silicon surface from reoxidation.

Results and discussion

Our strategy has been to functionalise the porphyrin ring on an available β -pyrrolic position in order to avoid the synthesis of a modified pyrrole precursor. Substitution by an azido function was



Fig. 1 Schematic representation of the grafting sequence. Reaction conditions: (i) nonadiyne, 140 °C, 12 h and (ii) nickel(II) β -azido-*meso*-tetraphenylporphyrin, CuSO₄·5H₂O, ascorbic acid, dry DMF, 50 °C, 17 h.

^aCEA-LETI, Département d'Intégration Hétérogène Silicium, Laboratoire Intégration Mémoires et Nanodispositifs, 17 rue des Martyrs, 38054, Grenoble Cedex 9, France

^bCEA-DSM, Institut Nanosciences et Cryogénie, Service de Chimie Inorganique et Biologique (UMR E-3 CEA-UJF), 17 rue des Martyrs, 38054, Grenoble Cedex 9, France. E-mail: florence.duclairoir@cea.fr

deemed more convenient than by an alkyne function. Therefore the linker had to contain at least one terminal alkyne for the cycloaddition reaction, and an aliphatic α, ω -diyne was selected to avoid the formation of multiple reaction products.

(a) Synthesis

The β -substituted azidoporphyrin was synthesised following a procedure recently reported for NiTPP **1** (see ESI[†]).¹¹ The first step is the efficient mono-nitration of the porphyrinic core on a β -position using Cu(NO₃)₂ in acetic anhydride.^{11,12} Reduction of the nitro derivative **2** using a Sn/HCl procedure provides the amino derivative **3** in a second step. The β -azidotetraphenylporphyrin **4** is finally obtained in good yield (85%) after diazotization by H₂SO₄/NaNO₂ and subsequent *in situ* reaction with NaN₃.

We then checked the feasibility of a cycloaddition reaction between the azidoporphyrin species and an aliphatic alkyne in solution. The click reaction worked in more than 80% yield using Cu¹ *in situ* generated by CuSO₄ and ascorbic acid in dry DMF (Scheme 1).^{6a,6c,10,13}

The electrochemical behaviour of 4 and 5 was studied in order to provide a reference for comparison with the results obtained for the immobilised species. The cyclic voltammogram (Fig. 2(a)) obtained for 4 exhibits two reversible redox waves in oxidative scan at $E_{1/2}^{1} = 0.754$ V and $E_{1/2}^{2} = 0.966$ V corresponding to the formation of the cation radical and dication of the porphyrin respectively. For 5, the cyclic voltammogram also exhibits two peaks at $E_{1/2}^{1} = 0.692$ V and $E_{1/2}^{2} = 0.970$ V; however the first oxidation potential is lower by ca. 60 mV than that of 4. The first oxidation potential is known to decrease linearly with respect to the substituent Hammett coefficient,^{12a} and the observed effect is consistent with a substitution change from azide to triazole that is more electron-withdrawing.^{12a,14} It is also apparent on the voltammogram of 5 that the second redox wave is less reversible, which is consistent with the presence of a bulky β -substituent that can interact with the meso-substituent leading to a deviation from planarity of the porphyrinic core.^{12a} The triazole ring of 5 is bulkier than the azide substituent of 4, and as shown by 2D



Fig. 2 Cyclic voltammograms of compounds 4 (a) and 5 (b) in oxidative scan (scan rate 100 mV s^{-1}).

¹H NMR analysis (data not shown) it does interact with a *meso*phenyl substituent. The planarity of the core is certainly affected and the dicationic species becomes harder to obtain ($\Delta E^1 - E^2$ for $5 > \Delta E^1 - E^2$ for 4) and is less stable hence the less reversible back wave.

(b) Surface grafting

Reaction of nonadiyne with surface 1 (hydrogenated silicon) led to immobilisation of the linker. In the infrared spectrum of the obtained surface 2 (Fig. 3(a)), two bands were observed at 2926 and 2854 cm⁻¹, which is in accordance with symmetric and



Scheme 1 Reaction conditions: (i) $Cu(NO_3)_2 \cdot 3H_2O$, $(CH_3CO)_2O$, rt, 3 h; (ii) Sn/HCl, $CHCl_3$, rt, 2 h; (iii) (a) $NaNO_2$, H_2SO_4 , $THF-H_2O$, rt, 30 min; (b) NaN_3 , H_2O , rt, 30 min; (iv) nonadiyne, $CuSO_4 \cdot 5H_2O$, ascorbic acid, DMF, 50 °C, 24 h.



Fig. 3 MIR-IR spectra of surface 2 after linker immobilisation (a), and of surface 3 after porphyrin coupling (b).

anti-symmetric methylene stretches.¹⁵ The band at 3303 cm⁻¹ was ascribed to the terminal alkyne.¹⁶ Ellipsometry data (Fig. 4(a)) indicate a layer thickness (12.8 Å) which is in good agreement with the expected thickness of a nonane monolayer (*ca.* 11 Å). These results show that polymerization of the terminal alkyne has not occurred and that only one terminal C=C triple bond of the linker has reacted with the surface. The XPS spectrum of surface **2** showed that the substrate was not contaminated by elements other than those expected (see ESI†). The C 1s spectrum did not allow discrimination between sp³, sp² and sp C atoms. The Si



Fig. 4 Table of the ellipsometry values obtained after linker grafting and porphyrin coupling (a), AFM image of the surface **2** after linker grafting (b), and of surface **3** after porphyrin coupling (c).

2p spectrum did not reveal a significant oxidation of the substrate (see ESI[†]), which indicated that the grafted monolayer was densely packed and prevented substrate oxidation by air.

Click reaction of surface 2 was performed under the conditions tested for 4 with nonadiyne in solution. The infrared spectra of surface 3 showed that the characteristic band (3303 cm⁻¹) for C–H vibration of the terminal alkyne had disappeared (Fig. 3(b)), consistent with the formation of a triazole, while around 1600 cm⁻¹ a signal appeared that can be ascribed to the phenyl substituents of the immobilised porphyrin, and which is very similar to that of porphyrin 5 (see ESI[†]).

The XPS spectrum of surface **3** revealed the presence of all the elements expected for the porphyrin-terminated monolayer (see ESI[†]). More importantly, the presence of the N 1s (Fig. 5(a)) and Ni $2p_{3/2}$ (Fig. 5(b)) confirmed that the porphyrin molecules were assembled on silicon surface. The Si 2p spectrum showed that the silicon substrate was oxidised by air, which might be due to the disruption of the linker monolayer by the large porphyrin molecules (see ESI[†]).



Fig. 5 N 1s HR XPS spectra (a), and Ni $2p_{3/2}$ (b) of surface 3, after porphyrin coupling.

On the high-resolution N 1s spectrum of the porphyrinterminated monolayer (Fig. 5(a)), the best fit was obtained when the signal is a composite of three peaks. The one at the lowest binding energy (399.5 eV) corresponds to the N signal of the nickel porphyrin. Previous studies have shown that for porphyrin free bases, both protonated and unprotonated Ns of the core can clearly be differentiated on the XPS spectra (in contrast to ¹H NMR spectroscopy that does not allow differentiation),¹⁹ while for a metalloporphyrin the Ns become equivalent and only one signal is visible in XPS, as observed for surface **3**. Recently, Zanoni *et al.* found that the value of the ΔBE (C 1s–N 1s) can help determining whether the N 1s signal observed corresponds to a free base ($\Delta BE = 113$ and 115 eV) or a complex ($\Delta BE = 114$ eV).²⁰



Fig. 6 Electrochemistry on surface 3 at different scan rates.

In the case of surface 3, $\Delta BE = 114$ eV which, as expected, is in good agreement with the N 1s signal of the complex. It is noteworthy that our grafting technique does not lead to demetallation of the metalloporphyrin, which was observed in a previous study.²⁰ Therefore in the present study a single porphyrin species is present on the surface. The two other N 1s signals at 400.9 eV and 402.1 eV are harder to assign as only one broad peak centred at 401 eV was expected for the N 1s of the triazole ring.^{5c,10b,10c} However literature examples and the 2:1 surface ratio observed after deconvolution of the peaks lead us to conclude that these signals belong to the chemically distinct N (sp³ and 2 sp^2) of the triazole ring. The surface ratios for the three N 1s signals are 4:2.1:1.2 which is close to that expected for the triazole substituted-metalloporphyrin. It is also important to notice that the signal of the azide function is neither visible on the XPS spectra (401 eV and 405 eV for the N 1s signals) nor on the MIR-IR spectra $(N_3 \text{ vibration at } 2100 \text{ cm}^{-1})$. This really confirms that the porphyrin derivative has been covalently immobilised on the surface and not only physisorbed.

Topographic analyses were also conducted on functionalised surface 3. It was found that the average thickness increased after the immobilisation of porphyrins in step 2 (Fig. 4). The experimental values determined by ellipsometry were a bit higher than the expected ones, but still remain in good accordance with the theoretical values and show that the porphyrins must be in upright position rather than flat on the surface. The AFM data are also consistent with this height increase. The RMS obtained for surface 3 is a little bit higher (0.52 Å) compared to the one obtained for surface 2 (0.31 Å); this might be due to site defects caused by the large volume of the porphyrin. Moreover as can be evidenced on the AFM image before (Fig. 4(b)) and after cycloaddition reaction (Fig. 4(c)), surface 2 is very smooth which is in good agreement with the absence of SiO₂ signal on the Si HR XPS spectra, whereas after porphyrin immobilisation, surface 3 is less homogeneous.²¹ Thus all the surface characterisation data show that the metalloporphyrin was successfully immobilised on Si(100).

Cyclic voltammetry experiments were also conducted to identify the impact of the surface confinement on the redox properties of the porphyrinic species. Fig. 6 shows the cyclic voltammograms of the porphyrin-functionalised surface 3. The oxidation wave for the cationic species was seen at $E_{1/2} = 1.26$ V, but the oxidation wave corresponding to the dicationic species formation was not detected, and it may be outside the solvent window. We also noticed that the current intensity is proportional to the scan rate (see ESI[†]) which is another clue confirming that the redox species is indeed immobilised on the surface. To further investigate the CV, the reference compounds 4 and 5 were studied for comparison (see above and ESI[†]). It was noticed that the first oxidation potential of the triazoloporphyrin 5 is much lower (0.692 V) than that of the porphyrin as surface species (1.26 V). This observation suggests that the linker monolayer and the presence of minute domains of reoxidised surface hamper the electron transfer from the porphyrin to the electrode. It is also clearly visible that going from an azide substituent to a triazole substituent has a profound effect on the second oxidation wave, as discussed above. It is therefore quite understandable that on the porphyrin-immobilised species this wave is not visible.

From the integration of the oxidised wave, the surface coverage of redox-active porphyrin was found to be close to $6 \times$ 10⁻¹¹ mol cm⁻². According to previous reports, this value reflects a medium coverage on Si(100).22 However, the electrochemical behaviour of surface 3 was irreproducible in some cases, especially when the click reaction was left to proceed for 48 h. We suppose that a change in density of surface molecules might be the cause of this fluctuation. Electron transfer might be slower when the surface coverage reaches saturation.^{23,24} Therefore it is important to control the distance between porphyrin units by targeting a medium coverage. Moreover, as explained in the literature recently, the choice of the counter-ion could have a profound impact on the redox response.²⁴ The larger the counter-ion, the harder it is for it to diffuse through the densely packed monolayer toward the working electrode, and the voltammograms obtained are less well defined.

Conclusion

We have described a click chemistry-based procedure for anchoring the macrocycle of nickel tetraphenylporphyrin on silicon. This technique is very efficient and simple to carry out. To the best of our knowledge, this is the first report of the covalent anchoring of a porphyrin on silicon using a substituent in β -pyrrolic position. With respect to the covalent attachment via a para-phenyl position of TPP, this procedure also offers the advantage of promoting electron transfer via the porphyrin edge, which presumably is faster than through a meso-phenyl substituent. We are in the process of trying new procedures that would minimize reoxidation of the silicon substrate, such as conducting these experiments in an inert atmosphere glove box, tuning the reaction time or using a linker as diluent to "fill" the holes between surface porphyrin species. Further experiments are also under way in our laboratory to explore the scope of this new method and its application to other linkers and molecules.

Experimental

Chemicals and reagents

Solvents and chemicals were used without purification unless indicated. Pyrrole was purified by filtration through basic alumina before use. The reactions were conducted under Ar, but no specific care was really taken in deaerating the solvent and drying the glassware unless otherwise stated. Dichloromethane stabilised over amylene (10 ppm) was used. Silica gel (MCL-Chrom, Merck; 70–230 mesh) was used for column chromatography.

Silicon samples

The nature and size of the silicon sample were selected depending on which characterisation technique was to be used. For MIR-IR analysis, the Si sample must be double sided polished, low doped and quite long (roughly $1 \times 8 \text{ cm}^2$, $\sim 10^{15}$ B atoms cm⁻³) to maximize the number of internal reflections. For XPS, AFM and ellipsometry analyses, a sample of $1.5 \times 2 \text{ cm}^2$ is sufficient. For the electrochemical measurements, a highly p-doped Si sample ($1.5 \times 2 \text{ cm}^2$, $\sim 2 \times 10^{19}$ B atoms cm⁻³) bearing a Au wire for the electrical contact has been used.

Instruments used for compound characterisation

The synthesised products were characterised using mainly: (i) UVvis spectra that were recorded on a Perkin-Elmer Lambda 9 UVvis-NIR spectrophotometer, (ii) IR-spectra that were recorded on a Perkin-Elmer 1600 FT-IR spectrometer, (iii) ¹H NMR spectra that were recorded on Bruker Avance 200 MHz or 500 MHz spectrometers using the residual solvent peak as an internal reference, (iv) mass spectra that were recorded in positive mode on a Quattro 2 (Micromass) electrospray mass spectrometer and (v) the electrochemical studies that were conducted using a PAR 283 unit from EG & G Princeton Applied Research controlled by a computer with the EG & G software. The electrochemical studies in solution were conducted using CH_2Cl_2 as solvent, NBu_4PF_6 1 M as electrolyte salt. The working electrode was a Pt disk. The counter electrode was a Pt wire and the reference electrode was Ag/Ag^+ .

Instruments used for functionalised surface characterisation

FTIR spectroscopy was performed on a Bruker IFS-55 spectrometer equipped with a MCT detector and a home-made MIR sample holder. The Multiple Internal Reflection set up consists in a work platform on which two silicon prism couplers are mounted. Two pressure tips supported by a clamping device allow a tight contact between the prisms and the silicon surface.

XPS spectra were recorded on an S-Probe spectrometer from Surface Science Instruments, equipped with a micro-focussed Al K α source monochromated at 1486.6 eV. Photoelectrons were detected at a take-off angle of 35° with respect to the sample surface by a hemispherical analyser, with an angular acceptance of 35° and pass energy of 25 eV. The overall energy resolution, resulting from monochromator band pass and electron analyser, was 700 meV. Binding energies (*BE*) are given relative to the Fermi level by subtracting the spectrometer work function measured with a clean gold surface (4f_{7/2} peak at 83.96 eV). Quantification of the detected species was made using the Scofield photo-ionization cross sections and the analyser transmission function.

Ellipsometry measurements were performed on a VUV phase modulated spectroscopic ellipsometer from Horiba Jobin Yvon. Spectra were recorded between 1.5 and 8 eV, in steps of 0.02 eV and the angle of incidence was set at 70° .

For the electrochemical studies the equipment also consisted of a PAR 283 unit from EG & G Princeton Applied Research controlled by a computer with the EG & G software. For the electrochemical studies purpose the active area of the Si working electrode was ~0.5 cm². The potentials are given *versus* the Ag/ (10 mM) Ag⁺ reference electrode and the counter electrode is a Pt wire. The electrolyte is a NBu₄PF₆ solution (0.1 M) in acetonitrile. Acetonitrile was distilled over P₂O₅ and NBu₄PF₆ dutifully dried. The cell was purged with Ar and prior to the analysis the solution was bubbled with Ar in order to exclude O₂.

Syntheses

The synthesis of **4** was performed using a procedure described by Shen *et al.*¹¹

Nickel(11)-2-[4-(hept-6-ynyl)-1,2,3-triazolo]-5,10,15, 20-tetraphenylporphyrin, 5

To a solution of **4** (17 mg, 0.25 mmol), CuSO₄·5H₂O (1 mg, 0.02 mmol) and ascorbic acid (3 mg, 0.12 mmol) in 4 mL of DMF was added 1,8-nonadiyne (30 mg, 2.5 mmol). The reaction mixture was stirred at 50 °C for 24 h. CH₂Cl₂ was added, and the organic phase was washed with aqueous K₂CO₃ and water, and dried with anhydrous Na₂SO₄. The solvent was removed under vacuum, and the residue was purified by column chromatography (CH₂Cl₂: petroleum ether, 2 : 1) to give the desired product (14 mg, 82%). λ (CH₂Cl₂, nm): 419, 533, 572. ν (cm⁻¹): 3288, 2957, 2918, 2849, 1682, 1597, 1527. ¹H NMR (500 MHz, CDCl₃): δ 8.93 (s, 1H, H^β–pyrrole in α triazole ring), 8.18–8.71 (m, 4H, H^β–pyrrole), 8.63 (d, J = 5 Hz, 1H, H^β–pyrrole), 8.45 (d, J = 5 Hz, 1H, H^β–pyrrole), 7.72–7.62 (m, 9 + 2H, H–Ph), 7.41 (t, $J \sim 7.5$ Hz, 1H, H–Ph), 7.32 (t, $J \sim 7.5$ Hz, 2H, H–Ph), 6.95 (s, 1H, H–triazole ring), 2.53 (t, $J \sim 7.8$ Hz, 2H, CH₂ in α

triazole ring), 2.23 (td, $J \sim 7.8$ Hz, $J \sim 2.5$ Hz, 2H, CH₂ in β of \equiv CH), 1.95 (t, $J \sim 2.5$ Hz, 1H, \equiv CH), 1.7–1.5 (m, 6H, 3 CH₂). MS (ESI) m/z: 832 (M + H⁺).

Functionalisation procedures

Step 1: formation of the alkyne-terminated Si(100) surface (surface 2). The silicon sample was first rinsed with acetone and ethanol. It was then dipped in hot piranha solution ($100 \degree C$, 1 vol 30% by weight aqueous hydrogen peroxide to 2 vol sulfuric acid) and etched in HF solution (1 vol 40% by weight hydrofluoric acid diluted with 5 vol water). After 3 piranha–HF cycles, the silicon wafer was transferred to a reaction vial containing freshly distilled 1,8-nonadiyne (which was degassed through a minimum of 4 freeze–pump–thaw cycles). The reaction vial was heated at 140 $\degree C$ overnight under a stream of argon. The functionalised surface was rinsed sequentially with copious amounts of chloroform, ethyl acetate and ethanol before being either analysed or further reacted with substituted azide species.

Step 2: preparation of the porphyrin-terminated Si(100) surface (surface 3). To a reaction vial containing the alkyne-terminated silicon surface (which was immersed in 10 mL of DMF) were added 4 (60 mg, 0.1 mmol), $CuSO_4 \cdot 5H_2O$ (2.5 mg, 0.01 mmol) and ascorbic acid (8 mg, 0.05 mmol). The reaction vial was heated at 50 °C for 24 h. The functionalised surface was rinsed sequentially with copious amounts of ethyl acetate, ethanol and water before being analysed.

Acknowledgements

We are grateful to Olivier Renault for XPS analyses, to Névine Rochat and Christophe Licitra for FTIR and ellipsometry analyses and to Pierre-Alain Bayle for NMR experiments. Support from the 'Carnot' program of the CEA-LETI is gratefully acknowledged.

References

- (a) K. M. Roth, A. A. Yasseri, Z. Liu, R. B. Dabke, V. Malinovskii, K.-H. Schweikart, L. Yu, H. Tiznado, F. Zaera, J. S. Lindsey, W. G. Kuhr and D. F. Bocian, J. Am. Chem. Soc., 2003, 125, 505; (b) Z. M. Liu, A. A. Yasseri, J. S. Lindsey and D. F. Bocian, Science, 2003, 302, 1543; (c) C. Li, J. Ly, B. Lei, W. Fan, D. Zhang, J. Han, M. Meyyappan, M. Thompson and C. Zhou, J. Phys. Chem. B, 2004, 108, 9646; (d) Q. Li, G. Mathur, S. Gowda, S. Surthi, Q. Zhao, L. Yu, J. S. Lindsey, D. F. Bocian and V. Misra, Adv. Mater., 2004, 16, 133; (e) L. Wei, D. Syomin, R. S. Loewe, J. S. Lindsey, F. Zaera and D. F. Bocian, J. Phys. Chem. B, 2005, 109, 6323; (f) C. B. Winkelmann, I. Ionica, X. Chevalier, G. Royal, C. Bucher and V. Bouchiat, Nano Lett., 2007, 7, 1454.
- 2 (a) A. R. Pease, J. O. Jeppesen, J. F. Stoddart, Y. Luo, C. P. Collier and J. R. Heath, Acc. Chem. Res., 2001, 34, 433; (b) J. E. Green, J. W. Choi, A. Boukail, Y. Bunimovich, E. Johnston-Halperin, E. Delonno, Y. Luo, B. A. Sheriff, K. Xu, Y. Shik Shin, H.-R. Tseng, J. F. Stoddart and J. R. Heath, Nature, 2007, 445, 414; (c) N. Weibel, S. Grunder and M. Mayor, Org. Biomol. Chem., 2007, 5, 2343; (d) N. Katsonis, M. Lubomska, M. M. Pollard, B. L. Feringa and P. Rudolf, Prog. Surf. Sci., 2007, 82, 407; (e) J. C. Scott and L. D. Bozano, Adv. Mater., 2007, 19, 1452.
- 3 (a) S. Gazeau, J. Pécaut and J.-C. Marchon, Chem. Commun., 2001, 1644; (b) G. Maheut, A. Castaings, J. Pécaut, L. M. Lawson Daku, G. Pescitelli, L. Di Bari and J.-C. Marchon, J. Am. Chem. Soc., 2006, 128, 6347.
- 4 Single-step immobilisation: (*a*) phosphonic acid substituent/SiO₂, K. Muthukumaran, R. S. Loewe, A. Ambroise, S.-I. Tamaru, Q. Li, G.

Mathur, D. F. Bocian, V. Misra and J. S. Lindsey, J. Org. Chem., 2004, 69, 1444; (b) alcohol or alkene substituent/surface Si–H, Z. Liu, A. A. Yasseri, R. S. Loewe, A. B. Lysenko, V. L. Malinovskii, Q. Zhao, S. Surthi, Q. Li, V. Misra, J. S. Lindsey and D. F. Bocian, J. Org. Chem., 2004, 69, 5568; (c) K. Padmaja, L. Wei, J. S. Lindsey and D. F. Bocian, J. Org. Chem., 2005, 70, 7972; (d) alkyne substituent polymerization, Z. Liu, I. Schmidt, P. Thamyongkit, R. S. Loewe, D. Syomin, J. R. Diers, Q. Zhao, V. Misra, J. S. Lindsey and D. F. Bocian, *Chem. Mater.*, 2005, 17, 3728; (e) diazonium salt/Si–H, M. Lu, B. Chen, T. He, Y. Li and J. M. Tour, *Chem. Mater.*, 2007, 19, 4447.

- 5 Multiple-step immobilisation: (a) G. Delapierre, F. Duclairoir and J.-C. Marchon, *French Pat.*, WO/2007/048924, Appl. 2005; Intl. Appl. No. PCT/FR2006/002395; (b) K. Huang, F. Duclairoir, T. Pro, J. Buckley, G. Marchand, E. Martinez, J.-C. Marchon, B. De Salvo, G. Delapierre and F. Vinet, *ChemPhysChem*10.1002/cphc/200800818.
- 6 (a) S. Ciampi, T. Böcking, K. A. Kilian, M. James, J. B. Harper and J. J. Gooding, *Langmuir*, 2007, **23**, 9320; (b) L. Britcher, T. J. Barnes, H. J. Griesser and C. A. Prestidge, *Langmuir*, 2008, **24**, 7625; (c) S. Ciampi, G. Le Saux, J. B. Harper and J. J. Gooding, *Electroanalysis*, 2008, **20**, 1513.
- 7 (a) J. M. Buriak, Chem. Soc. Rev., 2002, 102, 1271; (b) A. Faucheux, A.-C. Gouget-Laemmel, C. Henry de Villeneuve, R. Boukherroub, F. Ozanam, P. Allongue and J.-N. Chazalviel, Langmuir, 2006, 22, 153; (c) R. Zanoni, F. Cattaruzza, C. Coluzza, E. A. Dalchiele, F. Decker, G. Di Santo, A. Flamini, L. Funari and A. G. Marrani, Surf. Sci., 2005, 575, 260; (d) E. A. Dalchiele, A. Aurora, G. Bernardini, F. Cattaruzza, A. Flamini, P. Pallavicini, R. Zanoni and F. Decker, J. Electroanal. Chem., 2005, 579, 133; (e) S. N. Arafat, S. Dutta, M. Perring, M. Mitchell, P. J. A. Kenis and N. B. Bowden, Chem. Commun., 2005, 3198.
- 8 (a) R. Huisgen, Angew. Chem., Int. Ed. Engl., 1963, 2, 565; (b) H. C. Kolb, M. G. Finn and K. B. Sharpless, Angew. Chem., Int. Ed., 2001, 40, 2004.
- 9 (a) J. P. Collman, N. K. Devaraj, R. A. Decréau, Y. Yang, Y.-L. Yan, W. Ebina, T. A. Eberspacher and C. E. D. Chidsey, *Science*, 2007, 315, 1565; (b) J. P. Collman, N. K. Devaraj and C. E. D. Chidsey, *Langmuir*, 2004, 20, 1051; (c) N. K. Devaraj, G. P. Miller, W. Ebina, B. Kakaradov, J. P. Collman, E. T. Kool and C. E. D. Chidsey, *J. Am. Chem. Soc.*, 2005, 127, 8600; (d) J. P. Collman, N. K. Devaraj, T. P. A. Eberspacher and C. E. D. Chidsey, *Langmuir*, 2006, 22, 2457; (e) R. Zirbs, F. Kienberger, P. Hinterdorfer and W. H. Binder, *Langmuir*, 2005, 21, 8414; (f) J. K. Lee, Y. S. Chi and I. S. Choi, *Langmuir*, 2004, 20, 3844.
- 10 (a) T. Lummerstrofer and H. Hoffmann, J. Phys. Chem. B, 2004, 108, 3963; (b) A. G. Marrani, E. A. Dalchiele, R. Zanoni, F. Decker, F. Cattaruzza, D. Bonifazi and M. Prato, *Electrochim. Acta*, 2008, 53, 3903.
- 11 D.-M. Shen, C. Liu and Q.-Y. Chen, Eur. J. Org. Chem., 2007, 1419.
- 12 (a) H. K. Hombrecher, V. M. Gherdan and S. Ohm, *Tetrahedron*, 1993, 49, 8569; (b) A. Giraudeau, H. J. Callot, J. Jordan, I. Ezhar and M. Gross, J. Am. Chem. Soc., 1979, 101, 3857.
- 13 V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem.*, Int. Ed., 2002, 41, 2596.
- 14 (a) C. Hansch, A. Leo and R. W. Taft, *Chem. Soc. Rev.*, 1991, 91, 165; (b) S. J. Lord, N. R. Conley, H.-L. D. Lee, R. Samuel, N. Liu, R. J. Twieg and W. E. Moerner, *J. Am. Chem. Soc.*, 2008, 130, 9204.
- 15 (a) A. B. Sieval, A. L. Demirel, J. W. N. Nissink, M. R. Linford, J. H. van der Mass, W. H. de Jeu, H. Zuilhof and E. J. R. Sudhölter, *Langmuir*, 1998, 14, 1759; (b) M. R. Linford, P. Fenter, P. M. Eisenberger and C. E. D. Chidsey, J. Am. Chem. Soc., 1995, 117, 3145.
- 16 Although elucidation of the chemical nature of the Si–alkyne bonding was outside the scope of this work, we note that Si–H hydrosilylation of an alkyne may lead to a surface alkene or alkane if the latter further reacts with an adjacent Si–H group.^{7a} In our case the absence of C=C stretch in the IR spectrum of surface 2 suggests that a saturated linker is tethered to the surface by two Si–C bonds. Retention of a surface alkene has been reported when Si(111) or porous silicon were used,^{6b,17} but not for Si(100),^{6a,18} in agreement with the present data.
- 17 (a) M. R. Linford, P. Fenter, P. M. Eisenberger and C. E. D. Chidsey, J. Am. Chem. Soc., 1995, **117**, 3145; (b) J. M. Buriak and M. J. Allen, J. Am. Chem. Soc., 1998, **120**, 1339.
- 18 (a) A. B. Sieval, R. Opitz, H. P. A. Maas, M. G. Schoeman, G. Meijer, F. J. Vergeldt, H. Zuilhof and E. J. R. Sudhölter, *Langmuir*, 2000, **16**, 10359; (b) H. Liu and R. J. Hamers, *Surf. Sci.*, 1998, **416**, 354.

- 19 (a) H. Yamashige, S. Matsuo, T. Kurisaki, R. C. C. Perera and H. Wakita, Anal. Sci., 2005, 21, 635; (b) D. M. Sarno, L. J. Matienzo and W. E. Jones, Jr., Inorg. Chem., 2001, 40, 6308.
- 20 R. Zanoni, A. Aurora, F. Cattaruzza, F. Decker, P. Fastiggi, V. Menichetti, P. Tagliatesta, A.-L. Capodilupo and A. Lembo, Mater. Sci. Eng., C, 2007, 27, 1351.
- 21 The Si HR XPS spectra of this latest surface (see ESI[†]) indeed shows the presence of a SiO₂ peak and the AFM image recorded at a different

scale shows the presence of these SiO2 structures grown over the surface.

- 22 H. O. Finklea, in Encyclopedia of Analytical Chemistry, ed. R. A. Meyers, Wiley, Chichester, UK, 2000, pp. 1–26.
 23 K. M. Roth, D. T. Gryko, C. Clausen, J. Li, J. S. Lindsey, W. G. Kuhr
- and D. F. Bocian, J. Phys. Chem. B, 2002, 106, 8639.
- 24 J. Jiao, E. Nordlund, J. S. Lindsey and D. F. Bocian, J. Phys. Chem. C, 2008, 112, 6173.