Reversible photoswitching of stimuli-responsive Si(100) surfaces engineered with an assembled 1-cyano-1-phenyl-2-[4′-(10-undecenyloxy)phenyl]-ethylene monolayer

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Si(100) surfaces were molecularly engineered by covalent linkage of a monolayer of two stilbene-based chromophores, either 1-cyano-1-phenyl-2-[4′-(10-undecenyloxy)phenyl]-ethylene or its chlorine derivative, 1-cyano-1-(4-Cl-phenyl)-2-[4′-(10-undecenyloxy)phenyl]-ethylene. The hybrid systems have been probed by monochromatized angle-resolved X-ray photoelectron spectroscopy (AR-XPS) and atomic force microscopy (AFM) measurements. Results indicated robust covalent linkage of stilbene molecules to the functionalized substrate surfaces. AFM lithography and contact angle (CA) analysis confirmed that the adopted molecular architectures proved to be well-suited for reversible *cis–trans* photoswitching promoted by UV irradiation in the solid state.

Introduction

There is much current academic and industrial interest in the development of molecular films utilized as memory devices, sensors, switches and, in general, as stimuli-responsive materials (SRMs).[1,2] SRMs ideally undergo reversible changes in one or more properties (structure, phase morphology, electrical, magnetic and mechanical response, *etc.*) upon application/removal of an external stimulus, such as a change in temperature, ionic strength, pH, electric, magnetic or mechanical fields or by chemical, optical, or biological analytes. Such materials have potential smart applications in sensors, actuators, electro-optic devices, *etc.* In this context, the control of molecular structure and dynamics is of major importance from the perspective of designing SRM-based devices. The combination of optically responsive materials and monolayer assembly is a rapidly emerging field because these materials are inexpensive, miniature, robust and easy to fabricate.[3] Engineering of inorganic surfaces by covalent bonding of organic molecules also represents an interesting approach to the synthesis of hybrid inorganic–organic nanomaterials.[4] In this field, for instance, the large flexibility of porphyrins, fullerenes, and some inorganic complexes has been recently exploited by some researchers in order to assemble on SiO_2 a variety of functional materials capable of detecting various analytes by monolayer chemistry.[5] In this field, well-organized molecular structures covalently anchored to silicon[6] or other conducting substrates,[7] for facile integration within electronic circuits, can be pursued, to build molecularly based responsive materials in the perspective of fabricating opto-electronic devices.

Several recent studies on grafting of organic molecules on silicon surfaces focused on the Si(111) substrate because of the simple chemical etching procedure used to obtain atomically flat and chemically well-defined surfaces.[8] Moreover, it was also reported that it is possible to produce relatively flat Si(100) surfaces, predominantly SiH_2–terminated.[9] Various strategies can be adopted to anchor organic molecules to silicon. Among them, hydrosilation of molecular builders, functionalized with terminal multiple bonds, on hydrogen-terminated surfaces, remains the most suitable owing to the largest potential applications.[10]

The photochemistry and photophysics of stilbene and its derivatives have been extensively studied.[11,12] Stilbene molecules undergo photochemical *cis–trans* isomerization, dimerization, and cyclization reactions in solution.[11] Molecular switching processes are crucial to the realization of devices that can operate at both molecular and supramolecular levels.[2m] These stilbene molecules allow reversible modulation of electronic properties by external light triggering. Stilbene films have also been extensively studied in order to exploit their solid-state isomerization dynamics.[12] These thin films are generally obtained by sublimation,[13] spin coating,[14] or by the Langmuir–Blodgett[15] (LB) technique. With these techniques, the organization of the molecules within the film is difficult to control. Moreover, the resulting films are soluble in organic solvents. Recently, stilbene monolayers have also been obtained by self-assembly.[12b,e,f,h–j,l,m,o,p] This simple method relies on the covalent/non-covalent anchoring of the molecule on various substrates and results in great control of the molecular organization within the monolayer. Previous studies have revealed that the photochemistry of stilbene in the solid state[12b,g,j–l,n,o] and in micelles[11g] might differ from that in solution. In addition, the solid-state molecular environment is relevant for creating the properties needed in the photonic field. This interesting scenario prompted us to synthesize two novel cyano-stilbene systems with a molecular architecture that functions with covalent grafting on SiH_2-terminated Si(100) surfaces. This overall activity focuses on the development of a platform that will pave the way for direct photo-switching in

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the solid state, potentially useful for molecularly based information storage materials on Si surfaces. The monolayer response is based on AFM and contact angle monitoring.[8a,c,11g] Stable, reproducible responses upon repeated and alternating light radiation exposure has always been achieved with no degradation or material loss from the surface. Therefore, in this study, we report on the switching properties of the solid-state device, thus demonstrating the fabrication of a "photo-command" Si(100) surface.[3a] In addition, the synthesis, characterization, and covalent assembly of the novel stilbenes, (*Z*)-1-cyano-1-phenyl-2-[4′-(10-undecenyloxy)phenyl]-ethylene, hereafter (*Z*)-UCS, and its chlorine derivative, 1-cyano-1-(4-Cl-phenyl)-2-[4′-(10-undecenyloxy)phenyl]-ethylene, hereafter (*Z*)-UCS(Cl), are also described.

Experimental details

Aldrich grade reagents and solvents, used throughout all present syntheses, unless otherwise noted, were used as received. Solvents for substrate cleaning were distilled. Elemental analyses were performed using a Carlo-Erba 1106 model apparatus. Static TOF SIMS (Time of Flight Secondary Ions Mass Spectrometry) spectra were acquired in a static mode with a reflector-type spectrometer (ION-TOF TOFSIMS IV), using a pulsed $^{69}Ga^+$ primary ion beam (25 KeV, ~0.1 pA) rastered over a 300 × 300 μm² area. ^{1}H NMR spectra were recorded using a 500 MHz Varian Unity Inova spectrometer. Chemical shifts, which referred to the residue signal of the deuterated solvent (EtOH-d$_6$), were independent of concentration effects within the experimental concentration used ($1–5 \times 10^{-3}$ M). IR spectra were obtained with a Perkin-Elmer 1340 spectrophotometer. The thermal behavior of both (*Z*)-UCS and (*Z*)-UCS(Cl) was investigated by thermal gravimetric analysis under atmospheric pre-purified nitrogen, using a 2 °C min^{-1} heating rate in the 25–400 °C range. A Mettler Toledo TGA/SDTA 851 system was used. Samples of 6–8 mg were accurately weighed and examined in the 25–400 °C range.

Synthesis of 4-(10-undecenyloxy)benzaldehyde

4-Hydroxybenzaldehyde (0.5 g, 4.1 mmol), 1.14 g of 11-bromo-1-undecene (4.92 mmol), and 0.102 g of 18-crown-6 (0.41 mmol) were dissolved in 5 mL of acetone. After the addition of 0.85 g of potassium carbonate (6.1 mmol), the reaction mixture was stirred and refluxed for 24 h. Then, the mixture was cooled, filtered, and concentrated in vacuum. The resulting oil was subjected to column chromatography using CHCl$_3$ to afford the product as pale yellow oil (0.79 g, 2.9 mmol, 71% yield). ^{1}H NMR (CDCl$_3$): δ 9.88 (s, 1H), 7.83 (d, 2H), 6.99 (d, 2H), 5.82 (m, 1H), 4.96 (dd, 2H), 4.04 (t, 2H), 2.05 (dt, 2H), 1.82 (m, 2H), 1.47 (m, 2H), 1.28–1.42 (m, 10H).

Synthesis of (*Z*)-1-cyano-1-phenyl-2-[4′-(10-undecenyloxy)phenyl]-ethylene and (*Z*)-1-cyano-1-(4-Cl-phenyl)-2-[4′-(10-undecenyloxy)phenyl]-ethylene

(*Z*)-UCS and (*Z*)-UCS(Cl) were prepared by condensation of stoichiometric quantities of phenylacetonitrile or 4-Cl-phenylacetonitrile and 4-(10-undecenyloxy)benzaldehyde in ethanol with EtONa. (*Z*)-UCS: melting point: 41–42 °C (from EtOH). ^{1}H NMR (ethanol-d$_6$): δ 7.95 (d, 2H), 7.70 (d, 2H), 7.69 (s, 1H), 7.45 (t, 2H), 7.36 (t, 1H), 6.99 (d, 2H), 5.79 (m, 1H), 4.94 (dd, 2H), 4.05 (t, 2H), 2.05 (dt, 2H), 1.81 (m, 2H), 1.51 (m, 2H), 1.38–1.32 (m, 10H). IR (KBr): ν 2920, 2842, 2205, 1630, 1584, 1503, 1300, 1252, 1176, 905, 835 cm^{-1}. TOF SIMS *m*/*z* calcd for C$_{26}$H$_{31}$NO: 373.524; found = 373.321. Anal. calcd: C, 83.55; H, 8.38; N, 3.77, found C, 83.59; H, 8.32; N, 3.71. (*Z*)-UCS(Cl): melting point: 59–60 °C (from EtOH). ^{1}H NMR (EtOH-d$_6$): δ 7.96 (d, 2H), 7.75 (s, 1H), 7.70 (d, 2H), 7.45 (d, 2H), 7.01 (d, 2H), 5.78 (m, 1H), 4.94 (dd, 2H), 4.05 (t, 2H), 2.04 (dt, 2H), 1.81 (m, 2H), 1.51 (m, 2H), 1.28–1.42 (m, 10H). IR (KBr): ν 2920, 2840, 2210, 1635, 1590, 1510, 1460, 1300, 1255, 1185, 1090, 910, 830 cm^{-1}. TOF SIMS *m*/*z* calcd for C$_{26}$H$_{30}$ClNO: 407.975; found = 407.968. Anal. calcd: C, 76.47; H, 7.41; Cl, 8.73, N, 3.43, found C, 76.53; H, 7.36; Cl, 8.91; N, 3.49.

Monolayer formation and optical switching

For the fabrication of self-assembled monolayers, the Si(100) substrate was first cleaned with "piranha" solution (c H$_2$SO$_4$: 30% H$_2$O$_2$ 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 20 s, accurately dried with pre-purified N$_2$, and immediately placed in a stilbene-containing flask.[10a,16] In particular, 25 mg of (*Z*)-UCS or (*Z*)-UCS(Cl) were dissolved in 10 mL of anhydrous 1,3,5-trimethylbenzene (mesitylene). The stilbene systems were then refluxed at 160 °C for 2 h, under slow N$_2$ bubbling. After having been cooled to room temperature, the substrates were removed from the flask, rinsed, and repeatedly sonicated in dichloromethane, pentane, and toluene to remove any residual unreacted stilbene. This overall procedure has already proved to be effective in obtaining covalent grafting of alkene-terminated molecules on Si(100) surfaces.[8,9,10a,16] A blank test performed using Si(100) substrates not etched with HF, thus covered with an SiO$_2$ overlayer, gave no XPS evidence (*vide infra*) of grafted stilbene molecules. The obtained monolayer-bearing substrates are robust and remain intact, either after repetitive sonication, or upon the scotch tape de-cohesion test,[17] as evidenced by XPS measurements (*vide infra*). Air equilibrated ethanol (*Z*)-UCS and (*Z*)-UCS(Cl) solutions were irradiated (λ = 254 nm or 366 nm, 8 Watt) in quartz tubes, in a dark room, at room temperature to promote *cis–trans* isomerization. Stilbene monolayers were irradiated (λ = 254 nm or 366 nm, 8 Watt, 30 min each cycle).

Angle-resolved X-ray photoelectron spectra (AR-XPS) were measured at different takeoff angles (5°, 10°, 20°, 45°, 80°), relative to the surface plane, with a PHI 5600 Multi Technique System, which offers good control of the electron take-off angle (base pressure of the main chamber 2×10^{-10} Torr).[5,10a] The acceptance angle of the analyzer and the precision of the sample holder concerning the takeoff angle are ±3° and ±1°, respectively. 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 monochromatized Al–Kα radiation. The XPS peak intensities were obtained after Shirley background removal. 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.[10a] Some spectra were deconvoluted by fitting experimental profiles with a series of symmetrical Gaussian envelopes after subtracting the background. The agreement factor, $R = [\Sigma(F_0 - F_c)^2/\Sigma - (F_0)^2]^{½}$, after minimization of the function $\Sigma(F_0 - F_c)^2$ converged to R values ≤ 0.04.

Atomic force microscopy (AFM) measurements were performed with a Solver P47 NTD-MDT instrument in semi-contact mode (resonance frequency 150 Hz). The noise level before and after each measurement was confined within ±0.01 nm. Atomic force lithography was performed by rastering the AFM tip with a curvature radius of 10 nm under a constant force of 0.25 μN.

CA measurements were performed with a Kernco goniometer 10 min after the irradiation, at room temperature to exclude thermal effects. Two μL water drops were applied on the sample surface and measurements of the CA were made on both sides of the two-dimensional projection of the droplet. Every measurement was performed using 5 droplets on different surface portions of the substrate in order to have statistically reliable results. Differences in CA values of different droplets for every set of measurements were confined to a few decimals.

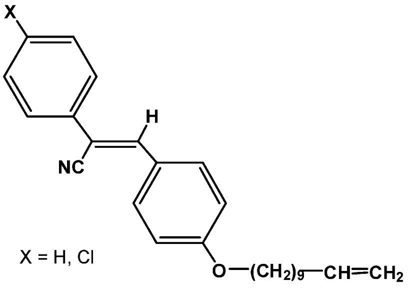

Fig. 1 Molecular structure of (*Z*)-UCS and (*Z*)-UCS(Cl).

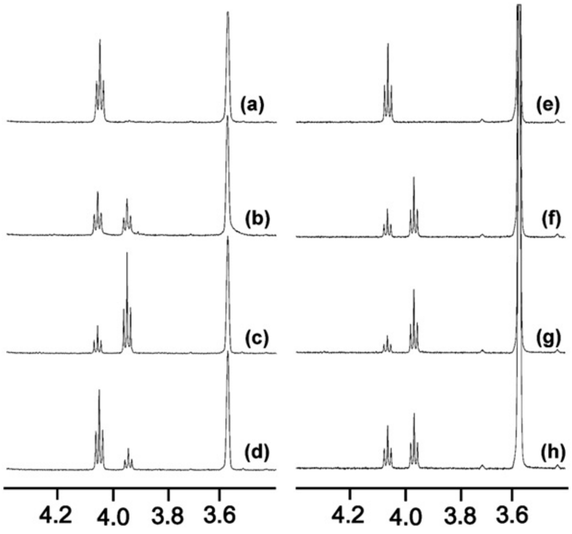

Fig. 2 ^{1}H-NMR spectra in the 3.4–4.3 ppm range. Lines (a), (b), (c) and (d) refer to UCS. Lines (e), (f), (g) and (h) refer to UCS(Cl). Specifically, (a) and (e) as synthesized (*Z*)-isomers; (b) and (f) after 10 min of irradiation at 366 nm; (c) and (g) after 30 min of irradiation at 366 nm; (d) and (h) after 30 min of irradiation at 254, nm subsequent to irradiation at 366 nm.

Results and discussion

The condensation reaction in alkaline medium between the appropriate aldehyde and the arylacetonitrile derivative produces cyanostilbenes in their *Z* configuration (>99%) (Fig. 1), consistent with ^{1}H-NMR spectra and both COSY and NOESY 2D map analyses. Air-equilibrated ethanol (*Z*)-UCS and (*Z*)-UCS(Cl) solutions undergo reversible photo-isomerization upon UV irradiation (λ = 254 or 366 nm) and changes are apparent in NMR spectra (Fig. 2).[11,12] In fact, upon illumination at 366 nm, a new set of slightly upfield-shifted resonances, arising from the aromatic, vinylic, and oxymethylene protons, become apparent, consistent with the (*E*)-isomer formation.[12n] Moreover, such an evolution parallels the fall-off of intensities due to the (*Z*)-isomer. Importantly, no photocyclized derivatives or photooxidized products have been detected by NMR spectroscopy, after irradiation at room temperature. This behavior is in good agreement with the presence of the electron-withdrawing cyano substituent on the vinyl moiety.[18] The 366 nm photostationary state shows a 1 : 3 (24% and 76%) (*Z*)-UCS : (*E*)-UCS, isomer ratio. Moreover, the present experiments showed that the (*E*)-UCS remains stable in the dark, at room temperature even for prolonged periods (10 days) and, therefore, the reverse (*E*)–(*Z*) isomerization can be photochemically switched. Irradiation with the shorter 254 nm UV wavelength recovers the (*Z*)-UCS isomer and the new 254 nm photostationary state reveals a reversed 3 : 1 (75% and 25%) (*Z*)-UCS : (*E*)-UCS isomer

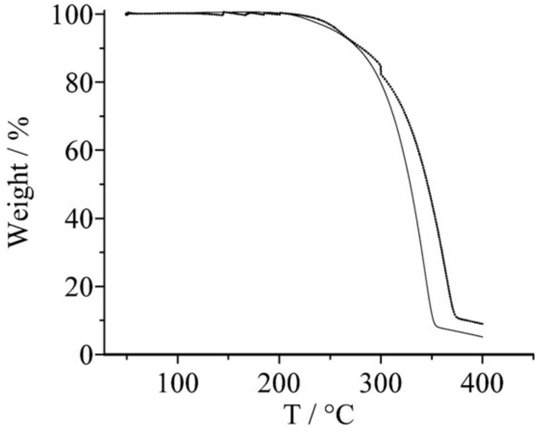

Fig. 3 TGA of (*Z*)-UCS (solid line) and (*Z*)-UCS(Cl) (dashed line) showing no weight loss up to 208 °C and 228 °C, respectively.

Table 1 XPS atomic concentration analysis of the Si(100)-UCS(Cl)-CAM. PTA = photoelectron take-off angle

PTA/°	Si 2p	O 1s	C 1s	N 1s	Cl 2p
80	27.8 (Si) + 4.1 (SiO_2) = 31.9	21.8	43.4	1.4	1.5
45	25.6 (Si) + 5.3 (SiO_2) = 30.9	21.0	45.0	1.5	1.6
20	14.0 (Si) + 5.8 (SiO_2) = 19.8	19.2	57.0	1.9	2.1
10	8.8 (Si) + 6.2 (SiO_2) = 15.0	17.7	62.8	2.2	2.3
5	3.1 (Si) + 8.3 (SiO_2) = 11.4	17.0	66.5	2.6	2.5

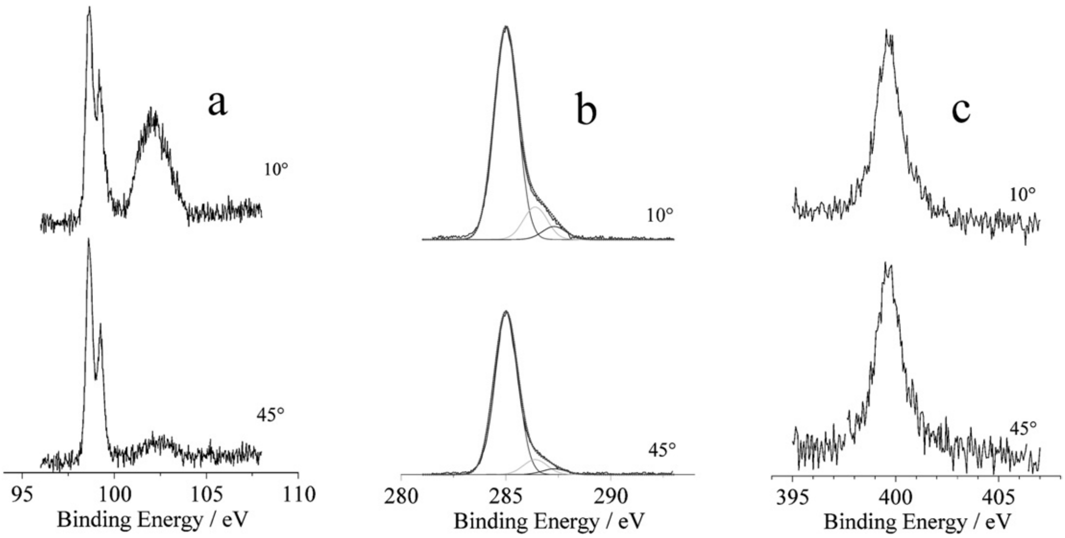

Fig. 4 Monochromatized Al Kα excited XPS of Si(100)-UCS(Cl)-CAM in (a) the Si 2p energy region; (b) the C 1s energy region (the dashed line, superimposed to the experimental profile, refers to the sum of the Gaussian components); (c) N 1s energy region.

ratio (Fig. 2(a)–(d)). NMR measurements provide evidence that irradiation times in the 1–30 min range force a progressive isomerization, whereas prolonged times (up to 1 h) do not significantly affect NMR spectra, as a consequence of the established *trans–cis* photostationary equilibrium. Photoisomerization experiments involving UCS(Cl) show a more efficient conversion towards a *cis* phostationary state (366 nm) with an 18% (*Z*) and 82% (*E*) ratio between the two isomers (Fig. 2(e)–(g)).

However, the reverse isomerization, to restore the *trans* state, is less efficient and results in 38% of (*Z*)-UCS(Cl) and 62% of (*E*)-UCS(Cl) (Fig. 2(h)). Upon switching between the 366 nm and 254 nm radiations, the ratio is 38–40% (*Z*) and, as a consequence, 62–60% (*E*).

The high thermal stability of both (*Z*)-UCS and (*Z*)-UCS(Cl) has been determined by thermal gravimetric analysis (TGA). (*Z*)-UCS remains stable up to 208 °C (Fig. 3). Beyond this range, it sublimates with an 8.1% residue left at 350 °C. Similar results have been obtained for (*Z*)-UCS(Cl), whose sublimation begins at 228 °C (Fig. 3). Both systems were found to be thermally stable beyond the temperature required for the synthesis of related monolayers (160 °C). In addition, both systems were heated at 160 °C for 2 h and then their NMR spectra checked again. No decomposition at all was observed. Self-assembled monolayers were synthesized using an already optimized one-step procedure that afforded covalent grafting of the stilbene units.[10a,16] Both Si(100)-supported (*Z*)-1-cyano-1-phenyl-2-[4′-(10-undecenyloxy) phenyl]-ethylene covalently assembled monolayer, hereafter Si(100)-UCS-CAM, and its chlorine derivative, (*Z*)-1-cyano-1-(4-Cl-phenyl)-2-[4′-(10-undecenyloxy)phenyl]-ethylene, hereafter Si(100)-UCS(Cl)-CAM, have been unambiguously characterized by X-ray photoelectron spectroscopy measurements.

This technique appears ideally suited since it provides high vertical resolution, using angle-resolved measurements, and gives

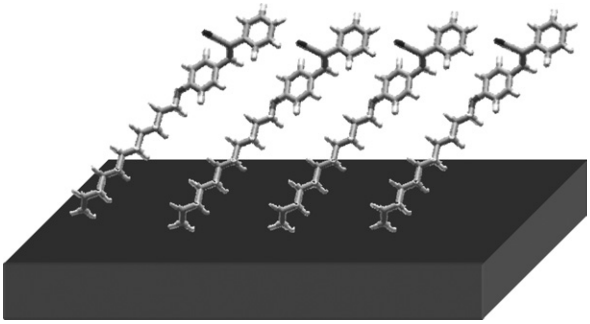

Fig. 5 Schematic representation of Si(100)-UCS-CAM.

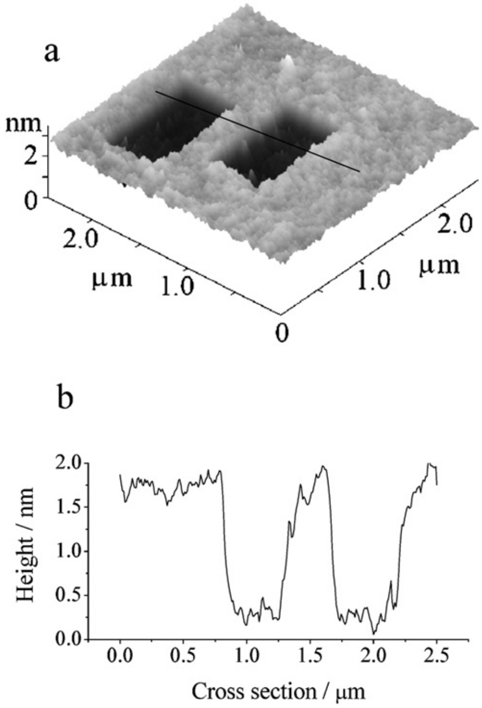

Fig. 6 AFM image (semi-contact mode) and cross section of a representative Si(100)-UCS-CAM.

information on the bonding states of the grafted molecules.[5,19] In this context, the presence of the additional Cl heteroatom on the chlorine derivative allows better characterization. Therefore, AR-XPS data of prototypical Si(100)-UCS(Cl)-CAM are here discussed.[20,21] Accumulating evidence suggests a decrease in both Si and O peaks, with a sizeable opposite trend for C, N, and Cl signals, at low photoemission angles (Table 1). In particular, the whole Si 2p signal (Fig. 4a) strongly decreases from 31.9 at 80° to 11.4% at a 5° photoelectron takeoff angle (PTA). The Si 2p feature is resolved into two components at 99.0 ($2p_{3/2}$) and 99.6 ($2p_{1/2}$) eV with a spin–orbit separation of 0.6 eV, in accordance with that expected for a Si(100) substrate.[10a] The broad band at 103.1 eV is consistent with the presence of some SiO_2.[10a] Therefore, the decreasing intensity trend of the whole Si 2p signal on a decrease of PTA is largely due to the fall-off of the Si(100) component since the SiO_2 peak, in contrast, shows a small increase. This overall observation points to some expected substrate surface oxidation already detected in similar systems.[10a] Analogously, the O 1s signal at 533.0 B.E. eV suffers an intensity decrease from 21.8 (at 80°) to 17.0% (at 5°).[8–10] Photoelectron spectra in the C 1s region (Fig. 4b) show a rich structure clearly because of several bonding states. There are three main components centered: i) at 285.0 eV due to both aliphatic and aromatic backbones,[22] ii) at 286.4 eV due to the carbon centers of the stilbene molecule bonded to the oxygen atom,[23] and, iii) at 287.4 eV due to the carbon of the –CN group.[23] Notably, the whole carbon atomic concentration significantly increases (43.4% *vs.* 66.5%) when passing from 80° to 5° PTA, with a more remarkable contribution of the higher (287.4 eV) energy component. Finally, the N 1s spectrum (Fig. 4c) exhibits a broad peak at 400.0 eV. This feature accounts for the nitrogen of the cyano group.[10a] The nitrogen atomic concentration also exhibits an appreciable increase upon decreasing the electron take-off angle from 1.4% (at 80°) to 2.6% (at 5°), as expected for the upper layer nature of the signal. Notably, the nitrogen : chlorine atomic concentration ratio always well matches the theoretical 1 : 1 value.

The film thickness, estimated using a model for an ideal planar structure with a homogeneous carbonaceous film of thickness *d*,

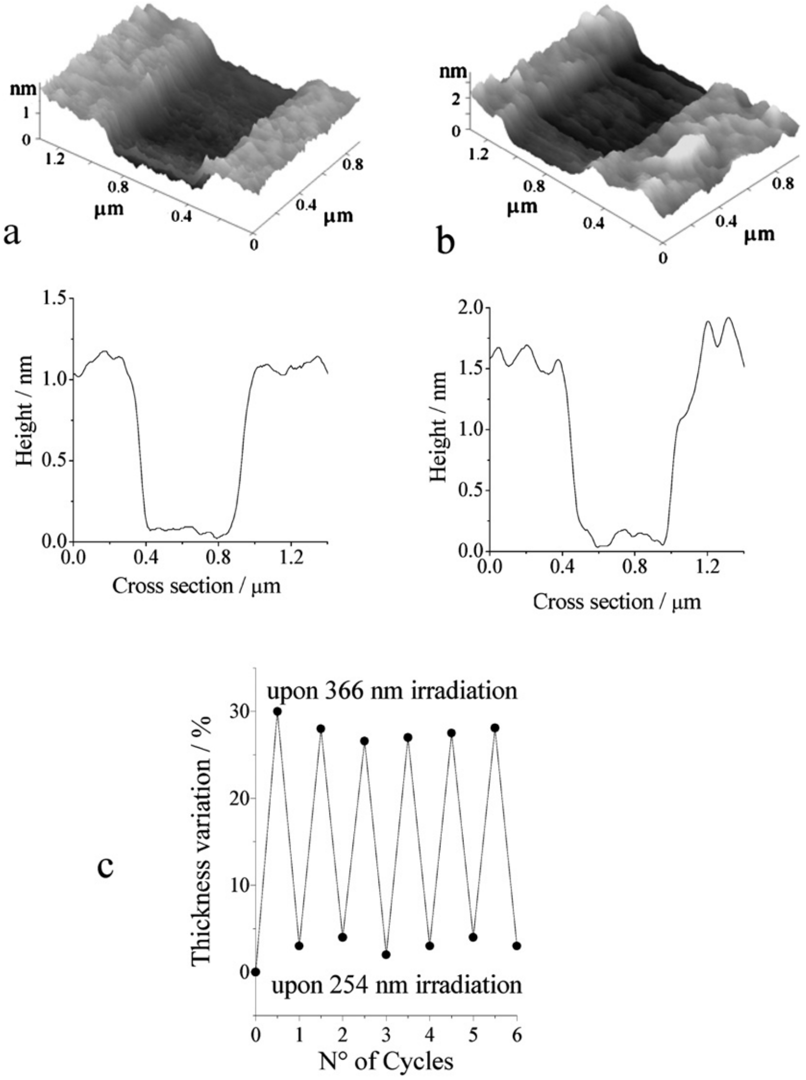

Fig. 7 AFM images (semi-contact mode) and cross sections of a representative Si(100)-UCS-CAM upon alternating AFM lithography *vs.* 30 min UV irradiation: (a) upon 366 nm, and (b) upon 254 nm irradiation; and (c) cycling irradiation and AFM measurements.

is 18 Å[12g] thus suggesting an inclined (*ca.* 45°) grafting geometry (Fig. 5) already observed in similar Si(100)-bonded monolayers (*vide infra*).[16] The estimated surface coverage with (*Z*)-UCS(Cl) molecules results in 8×10^{13} molecules cm^{-2} with a footprint of 150 Å per stilbene unit.[5b,21] In summary, the XPS technique has provided useful details particularly rich in unique chemical information not accessible using other, alternative spectroscopic techniques.

Fig. 6a shows a representative AFM image of the Si(100)-UCS-CAM. The surface morphology, obtained in semi-contact mode, appears homogeneous with a mean roughness of 0.088 nm. The thickness of the monolayer has been evaluated using AFM lithography (contact mode).[24] Thus, grafted molecules were removed along straight lines by rastering two different areas (both 0.5×1 μm in size) of the surface with the AFM tip under a suitable constant force. The two obtained scratch depths (Fig. 6b) are almost coincident and equal 1.7 ± 0.1 nm. This value approaches that obtained by XPS for the Si(100)-UCS(Cl)-CAM.

Dynamic surface changes owing to the *cis–trans* isomerization reaction can be monitored by AFM.[1c] The monolayer thickness variations in the Si(100)-UCS-CAM have been determined by alternating atomic force lithography *vs.* UV irradiation. Fig. 7a shows the observed thickness changes as a result of 366 nm light stimulus, followed by 254 nm (Fig. 7b) regeneration. The results indicate that the *cis* isomerization produces a $25 \pm 5\%$ decrease in thickness, followed by almost regeneration of the starting thickness upon irradiation at 254 nm. Taking into account the inclined grafting geometry already obtained by XPS measurements (*vide supra*), the observed thickness variation is in good agreement with results of MM + calculations on the two isomers whose sizes, (*Z*) (24.8 Å) and (*E*) (19.6 Å), differ by 21%. Cycling irradiation and AFM measurements (Fig. 7c) confirm reversible switching surface modifications. This observation is in agreement with literature data showing that the interfacial properties are defined by the molecular-level structure of the surface and can be monitored by AFM and CA analysis.[1c]

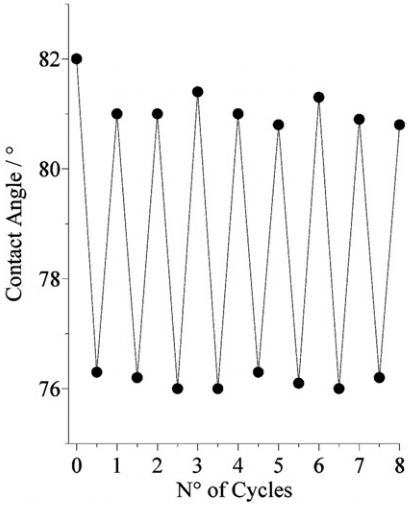

Fig. 8 Contact angles of Si(100)-UCS-CAM under alternating 30 min irradiation at 366 and 254 nm. CA values upon 30 min 366 nm irradiation lie in the 76.3°–76.0° range, whilst upon 30 min 254 irradiation they lie in the 81.4°–80.8° range. Experimental uncertainty ±1°.

The photoisomerization reaction of the present monolayer system on the Si(100) surface was also investigated by alternating irradiation at 366 and 254 nm with aqueous CA analysis.[11g,12a,c,p] Fig. 8 shows the monolayer performance/stability of the reversible photo-isomerized states demonstrated for 8 irradiation cycles.

The system remains stable under the adopted conditions. No hysteresis, relevant drift, or change in the output signal, independent of the input, has been observed for prolonged storage of the system in a dark room, at room temperature, after irradiation. Both photo-isomerized states remain stable in air for prolonged periods of time. The stilbene molecules immobilized on surfaces could suffer some steric hindrance that may partially hamper the reversible *cis–trans* photo-switching.[12b] The XPS-derived molecular footprint already excludes these interactions for the present Si(100)-UCS-CAM. Nevertheless, additional cleaned Si(100) substrates were immersed in a mesitylene solution containing a 1 : 9 (mol/mol) mixture of (*Z*)-UCS and decene, for the fabrication of diluted monolayers. It has already been demonstrated that the use of a 1-decene spectator spacer represents a suitable expedient for fabricating covalently assembled monolayers having a composition/dilution strongly reminiscent of that in solution.[16] XPS results (N 1s/C 1s band intensity) of the present mixed monolayer are indicative of 0.7 : 9 UCS : decene molecules on this "diluted" Si(100)-UCS-CAM. C.A. measurements on this system yielded variations similar to those already observed for the "undiluted" monolayer.

Conclusion

Both thickness variations and contact angle measurements unambiguously demonstrated the *cis–trans* solid state isomerization reaction of the new stilbene-based Si(100)-UCS-CAM, promoted by UV irradiation. Angle-resolved XPS measurements provided evidence that stilbene molecules were grafted on Si(100) substrates. In addition, two new stilbene systems, namely, 1-cyano-1-phenyl-2-[4′-(10-undecenyloxy)phenyl]-ethylene and its chlorine derivative, 1-cyano-1-(4-Cl-phenyl)-2-[4′-(10-undecenyloxy)phenyl]-ethylene, were synthesized and characterized. Finally, all these results indicate that this system is a good candidate for fabricating SRMs on silicon and, in general, is potentially useful for molecular-based devices that need direct photo-switching in the solid state.

Acknowledgements

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References

1 (*a*) S. Kobatake, S. Takami, H. Muto, T. Ishikawa and M. Irie, *Nature*, 2007, **446**, 778; (*b*) E. Baena-González, F. Rolland, J. M. Thevelein and J. Sheen, *Nature*, 2007, **448**, 938; (*c*) J. Lahann, S. Mitragotri, T.-N. Tran, H. Kaido, J. Sundaram, I. S. Choi, S. Hoffer, G. A. Somorjai and R. Langer, *Science*, 2003, **299**, 371; (*d*) F. Vera, R. M. Tejedor, P. Romero, J. Barber, M. B. Ros,

J. L. Serrano and T. Sierra, *Angew. Chem., Int. Ed.*, 2007, **46**, 1873; (*e*) S. P. Foxon, T. Phillips, M. R. Gill, M. Towrie, A. W. Parker, M. Webb and J. A. Thomas, *Angew. Chem., Int. Ed.*, 2007, **46**, 3686; (*f*) H. Liu, Y. Xu, F. Li, Y. Yang, W. Wang, Y. Song and D. Liu, *Angew. Chem., Int. Ed.*, 2007, **46**, 2515; (*g*) L. Li, H. Jiang, B. W. Messmore, S. R. Bull and S. I. Stupp, *Angew. Chem., Int. Ed.*, 2007, **46**, 5873; (*h*) D. Zehm, W. Fudickar and T. Linker, *Angew. Chem., Int. Ed.*, 2007, **46**, 7689; (*i*) S. Xiao, Y. Zou, M. Yu, T. Yi, Y. Zhou, F. Li and C. Huang, *Chem. Commun.*, 2007, 4758; (*j*) S. Kobatake and Y. Terakawa, *Chem. Commun.*, 2007, 1698; (*k*) D. Tuncel, Ö. Özsar, H. B. Tiftika and B. Salihb, *Chem. Commun.*, 2007, 1369; (*l*) H. Tian and S. Wang, *Chem. Commun.*, 2007, 781; (*m*) R. O. Al-Kaysi, J. L. Bourdelande, I. Gallardo, G. Guirado and J. Hernando, *Chem.–Eur. J.*, 2007, **13**, 7066; (*n*) Y. Liu, R. Hammitt, D. A. Lutterman, R. P. Thummel and C. Turro, *Inorg. Chem.*, 2007, **46**, 6011; (*o*) S. Saha, A. H. Flood, J. F. Stoddart, S. Impellizzeri, S. Silvi, M. Venturi and A. Credi, *J. Am. Chem. Soc.*, 2007, **129**, 12159; (*p*) M. C. Carreño, I. Garcìa, I. Núñez, E. Merino, M. Ribagorda, S. Pieraccini and G. P. Spada, *J. Am. Chem. Soc.*, 2007, **129**, 7089; (*q*) C. Schäfer, R. Eckel, R. Ros, J. Mattay and D. Anselmetti, *J. Am. Chem. Soc.*, 2007, **129**, 1488; (*r*) S. Silvi, A. Arduini, A. Pochini, A. Secchi, M. Tomasulo, F. M. Raymo, M. Baroncini and A. Credi, *J. Am. Chem. Soc.*, 2007, **129**, 13378; (*s*) A. L. Koner, J. Schatz, W. M. Nau and U. Pischel, *J. Org. Chem.*, 2007, **72**, 3889; (*t*) J. Rochford, A. D. Rooney and M. T. Pryce, *Inorg. Chem.*, 2007, **46**, 7247; (*u*) G. Guirado, C. Coudret and J. P. Launay, *J. Phys. Chem. C*, 2007, **111**, 2770; (*v*) J. J. de Jonge, M. A. Ratner and S. W. de Leeuw, *J. Phys. Chem. C*, 2007, **111**, 3770; (*w*) F. Fungo, M. E. Milanesio, E. N. Durantini, L. Otero and T. Dittrich, *J. Mater. Chem.*, 2007, **17**, 2107; (*x*) I. Vlassiouk, F. Rios, S. A. Vail, D. Gust and S. Smirnov, *Langmuir*, 2007, **23**, 7784; (*y*) F. A. Plamper, A. Walther, A. H. E. Müller and M. Ballauff, *Nano Lett.*, 2007, **7**, 167; (*z*) J. P. Malval, I. Leray and B. Valeurab, *New J. Chem.*, 2005, **29**, 1089.

2 (*a*) S. Zhang, C. M. Cardona and L. Echegoyen, *Chem. Commun.*, 2006, 4461; (*b*) R. V. Klitzing, *Phys. Chem. Chem. Phys.*, 2006, **8**, 5012; (*c*) R. Yerushalmi, A. Scherz, M. E. van der Boom and H.-B. Kraatz, *J. Mater. Chem.*, 2005, **15**, 4480; (*d*) O. Ihata, Y. Kayaki and T. Ikariya, *Chem. Commun.*, 2005, 2268; (*e*) L. Basabe-Desmonts, R. S. Zimmerman, D. N. Reinhoudt and M. Crego-Calama, *Springer Ser. Chem. Sens. Biosens.*, 2005, **3**, 169; (*f*) K. Yu, Y. Cong, J. Fu, R. Xing, N. Zhao and Y. Han, *Surf. Sci.*, 2004, **572**, 490; (*g*) J. Kappler, U. Weimar and W. Goepel, *Adv. Gas Sens.*, 2003, 55; (*h*) F. Raymo, *Adv. Mater.*, 2002, **14**, 401; (*i*) X. Duan, Y. Huang and C. M. Lieber, *Nano Lett.*, 2002, **2**, 487; (*j*) E. Galoppini, W. Guo, W. Zhang, P. G. Hoertz, P. Qu and G. J. Meyer, *J. Am. Chem. Soc.*, 2002, **124**, 7801; (*k*) D. C. Tully and J. M. J. Fréchet, *Chem. Commun.*, 2001, 1229; (*l*) M. Irie, *Chem. Rev.*, 2000, **100**, 1685; (*m*) I. Willner and E. Katz, *Angew. Chem., Int. Ed.*, 2000, **39**, 1181; (*n*) T. Weimar, *Angew. Chem., Int. Ed.*, 2000, **39**, 1219; (*o*) S. Flink, F. C. J. M. van Veggel and D. N. Reinhoudt, *Adv. Mater.*, 2000, **12**, 1315; (*p*) L. Fabbrizzi, M. Licchelli and P. Pallavicini, *Acc. Chem. Res.*, 1999, **32**, 846; (*q*) A. Fernández-Acebes and J.-M. Lehn, *Chem.–Eur. J.*, 1999, **5**, 3285; (*r*) R. M. Crooks and A. J. Ricco, *Acc. Chem. Res.*, 1998, **31**, 219.

3 (*a*) G. Wen, J. Yan, Y. Zhou, D. Zhang, L. Mao and D. Zhu, *Chem. Commun.*, 2006, 3016; (*b*) A. M. Moore, A. A. Dameron, B. A. Mantooth, R. K. Smith, D. J. Fuchs, J. W. Ciszek, F. Maya, Y. Yao, J. M. Tour and P. S. Weiss, *J. Am. Chem. Soc.*, 2006, **128**, 1959; (*c*) P. A. Lewis, C. E. Inman, F. Maya, J. M. Tour, J. E. Hutchison and P. S. Weiss, *J. Am. Chem. Soc.*, 2005, **127**, 17421; (*d*) Y. Liu, L. Mu, B. Liu and J. Kong, *Chem.–Eur. J.*, 2005, **11**, 2622; (*e*) Y. S. Chi, S. Hwang, B. S. Lee, J. Kwak, I. S. Choi and S.-g. Lee, *Langmuir*, 2005, **21**, 4268; (*f*) K. Critchley, J. P. Jeyadevan, H. Fukushima, M. Ishida, T. Shimoda, R. J. Bushby and S. D. Evans, *Langmuir*, 2005, **21**, 4554; (*g*) S. Jiang and M. Liu, *Chem. Mater.*, 2004, **16**, 3985; (*h*) M. L. Bushey, T.-Q. Nguyen and C. Nuckolls, *J. Am. Chem. Soc.*, 2003, **125**, 8264; (*i*) K. Tamada, H. Akiyama and T. X. Wei, *Langmuir*, 2002, **18**, 5239; (*j*) E. W. Wong, C. P. Collier, M. Běhloradský, F. M. Raymo, J. F. Stoddart and J. R. Heath, *J. Am. Chem. Soc.*, 2000, **122**, 5831; (*k*) I. Willner and B. Willner, *J. Mater. Chem.*, 1998, **8**, 2543.

4 (*a*) M. Altman, A. D. Shukla, T. Zubkov, G. Evmenenko, P. Dutta and M. E. van der Boom, *J. Am. Chem. Soc.*, 2006, **128**, 7374; (*b*) T. Gupta, M. Altman, A. D. Shukla, D. Freeman, G. Leitus and M. E. van der Boom, *Chem. Mater.*, 2006, **18**, 1379; (*c*) J. F. Fernández-Sánchez, T. Nezel, R. Steiger and U. E. Spichiger-Keller, *Sens. Actuators, B*, 2006, **113**(14), 630; (*d*) M.-S. Chen, C. S. Dulcey, L. A. Chrisey and W. J. Dressick, *Adv. Funct. Mater.*, 2006, **16**, 774; (*e*) H. Dacres and R. Narayanaswamy, *Sens. Actuators, B*, 2005, **107**, 14; (*f*) A. Facchetti, E. Annoni, L. Beverina, M. Morone, P. Zhu, T. J. Marks and G. A. Pagani, *Nat. Mater.*, 2004, **3**, 910; (*g*) 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; (*h*) H. Yamada, H. Imahori, Y. Nishimura, I. Yamazaki, T. K. Ahn, S. K. Kim, D. Kim and S. Fukuzumi, *J. Am. Chem. Soc.*, 2003, **125**, 9129; (*i*) T. van der Boom, G. Evmenenko, P. Dutta and M. R. Wasielewski, *Chem. Mater.*, 2003, **15**, 4068; (*j*) Z. Liu, A. A. Yasseri, J. S. Lindsey and D. F. Bocian, *Science*, 2003, **302**, 1543; (*k*) A. Facchetti, A. Abbotto, L. Beverina, M. E. van der Boom, P. Dutta, G. Evmenenko, G. A. Pagani and T. J. Marks, *Chem. Mater.*, 2003, **15**, 1064; (*l*) P. Samori, V. Francke, V. Enkelmann, K. Muellen and J. P. Rabe, *Chem. Mater.*, 2003, **15**, 1032; (*m*) J. H. Fendler, *Chem. Mater.*, 2001, **13**, 3196; (*n*) P. Gomez-Romero, *Adv. Mater.*, 2001, **13**, 163; (*o*) J. Cui, A. Wang, N. L. Edleman, J. Ni, P. Lee, N. R. Armstrong and T. J. Marks, *Adv. Mater.*, 2001, **13**, 1476.

5 (*a*) A. Gulino, T. Gupta, P. G. Mineo and M. E. van der Boom, *Chem. Commun.*, 2007, 4878; (*b*) A. Gulino, P. Mineo and I. Fragalà, *J. Phys. Chem. C*, 2007, **111**, 1373; (*c*) A. Gulino, S. Giuffrida, P. Mineo, M. Purrazzo, E. Scamporrino, G. Ventimiglia, M. E. van der Boom and I. Fragalà, *J. Phys. Chem. B*, 2006, **110**, 16781; (*d*) A. Gulino, P. Mineo, E. Scamporrino, D. Vitalini and I. Fragalà, *Chem. Mater.*, 2006, **18**, 2404; (*e*) A. Gulino, G. G. Condorelli, P. Mineo and I. Fragalà, *Nanotechnology*, 2005, **16**, 2170; (*f*) A. Gulino, G. P. Mineo, S. Bazzano, D. Vitalini and I. Fragalà, *Chem. Mater.*, 2005, **17**, 4043; (*g*) A. Gulino, S. Bazzano, P. Mineo, E. Scamporrino, D. Vitalini and I. Fragalà, *Chem. Mater.*, 2005, **17**, 521; (*h*) A. Gulino, P. Mineo, E. Scamporrino, D. Vitalini and I. Fragalà, *Chem. Mater.*, 2004, **16**, 1838.

6 (*a*) G. G. Condorelli, A. Motta, M. Favazza, I. L. Fragalà, M. Busi, E. Menozzi, E. Dalcanale and L. Cristofolini, *Langmuir*, 2006, **22**, 11126; (*b*) M. Busi, M. Laurenti, G. G. Condorelli, A. Motta, M. Favazza, I. L. Fragalà, M. Montalti, L. Prodi and E. Dal Canale, *Chem.–Eur. J.*, 2007, **13**, 6891; (*c*) L. Wei, D. Syomin, R. S. Loewe, J. S. Lindsey, F. Zaera and D. F. Bocian, *J. Phys. Chem. B*, 2005, **109**, 6323; (*d*) 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*) Y. Otsuka, Y. Naitoh, T. Matsumoto, W. Mizutani, H. Tabata and T. Kawai, *Nanotechnology*, 2004, **15**, 1639; (*f*) Y. Wakayama, T. Kubota, H. Suzuki, T. Kamikado and S. Mashiko, *Nanotechnology*, 2004, **15**, 1446; (*g*) U. Weiler, T. Mayer, W. Jaegermann, C. Kelting, D. Schlettwein, S. Makarov and D. J. Wöhrle, *J. Phys. Chem. B*, 2004, **108**, 19398; (*h*) A. A. Yasseri, D. Syomin, R. S. Loewe, J. S. Lindsey, F. Zaera and D. F. Bocian, *J. Am. Chem. Soc.*, 2004, **126**, 15603; (*i*) O. Gershevitz and C. N. Sukenik, *J. Am. Chem. Soc.*, 2004, **126**, 482; (*j*) O. Gershevitz, C. N. Sukenik, J. Ghabboun and D. Cahen, *J. Am. Chem. Soc.*, 2003, **125**, 4730.

7 (*a*) J. M. Gottfried, K. Flechtner, A. Kretschmann, T. Lukasczyk and H.-P. Steinrück, *J. Am. Chem. Soc.*, 2006, **128**, 5644; (*b*) A. A. Yasseri, D. Syomin, V. L. Malinovskii, R. S. Loewe, J. S. Lindsey, F. Zaera and D. F. Bocian, *J. Am. Chem. Soc.*, 2004, **126**, 11944; (*c*) S. Sortino, S. Petralia, S. Conoci and S. Di Bella, *J. Mater. Chem.*, 2004, **14**, 811; (*d*) Z. Zhang, S. Hou, Z. Zhu and Z. Liu, *Langmuir*, 2000, **16**, 537.

8 (*a*) X. Wallart, C. H. de Villeneuve and P. Allongue, *J. Am. Chem. Soc.*, 2005, **127**, 7871–7878; (*b*) Y.-J. N. M. Liu, Navasero and H.-Z. Yu, *Langmuir*, 2004, **20**, 4039–4050; (*c*) H. Jin, C. R. Kinser, P. A. Bertin, D. E. Kramer, J. A. M. C. Libera, Hersam, S. T. Nguyen and M. J. Bedzyk, *Langmuir*, 2004, **20**, 6252–6258; (*d*) A. Bansal, X. Li, S. I. Yi, W. H. Weinberg and N. S. Lewis, *J. Phys. Chem. B*, 2001, **105**, 10266–10277; (*e*) T. Strother, W. Cai, X. Zhao, R. J. Hamers and L. M. Smith, *J. Am. Chem. Soc.*, 2000, **122**, 1205; (*f*) M. R. Linford, P. Fenter,

P. M. Eisenberg and C. E. D. Chidsey, *J. Am. Chem. Soc.*, 1995, **117**, 3145–3155.

9 (*a*) Y. J. Chabal, G. S. Higashi, K. Raghavachari and A. V. Burrows, *J. Vac. Sci. Technol., A*, 1989, **7**, 2104; (*b*) G. F. Cerofolini, C. Galati, G. Giorgi, A. Motta, S. Reina, L. Renna and A. Terrasi, *Appl. Phys. A: Mater. Sci. Process.*, 2005, **A81**, 745.

10 (*a*) A. Gulino, F. Lupo, G. G. Condorelli, P. Mineo and I. Fragalà, *Chem. Mater.*, 2007, **19**, 5102; (*b*) G. F. Cerofolini, C. Galati, S. Reina, L. Renna, G. G. Condorelli, I. L. Fragalà, G. Giorgi, A. Sgamellotti and N. Re, *Appl. Surf. Sci.*, 2005, **246**, 52; (*c*) Q.-Y. Sun, L. C. P. M. de Smet, B. van Lagen, M. Giesbers, P. C. Thune, J. van Engelenburg, F. A. de Wolf, H. Zuilhof and E. J. R. Sudholter, *J. Am. Chem. Soc.*, 2005, **127**, 2514; (*d*) A. B. Sieval, A. L. Demirel, J. M. Nissink, M. R. Linford, J. H. van der Maas, W. H. de Jeu, H. Zuilhof and E. J. R. Sudhölter, *Langmuir*, 1998, **14**, 1759.

11 (*a*) F. D. Lewis, L. E. Sinks, W. Weigel, M. C. Sajimon and E. M. Crompton, *J. Phys. Chem. A*, 2005, **109**, 2443; (*b*) B. Durbeej and L. A. Eriksson, *J. Phys. Chem. A*, 2005, **109**, 5677; (*c*) F. Lincker, P. Bourgun, P. Masson, P. Didier, L. Guidoni, J.-Y. Bigot, J.-F. Nicoud, B. Donnio and D. Guillon, *Org. Lett.*, 2005, **7**, 1505; (*d*) J.-S. Yang, K.-L. Liau, C.-M. Wang and C.-Y. Hwang, *J. Am. Chem. Soc.*, 2004, **126**, 12325; (*e*) S. P. Gromov, E. N. Ushakov, O. A. Fedorova, I. I. Baskin, A. V. Buevich, E. N. Andryukhina, M. V. Alfimov, D. Johnels, U. G. Edlund, J. K. Whitesell and M. A. Fox, *J. Org. Chem.*, 2003, **68**, 6115; (*f*) E. N. Ushakov, S. P. Gromov, A. I. Vedernikov, E. V. Malysheva, A. A. Botsmanova, M. V. Alfimov, B. Eliasson, U. G. Edlund, J. K. Whitesell and M. A. Fox, *J. Phys. Chem. A*, 2002, **106**, 2020; (*g*) J. Eastoe, M. Sanchez Dominguez, P. Wyatt, A. Beeby and R. K. Heenan, *Langmuir*, 2002, **18**, 7837; (*h*) F. D. Lewis, R. S. Kalgutkar and J.-S. Yang, *J. Am. Chem. Soc.*, 2001, **123**, 3878; (*i*) J. Catalán, L. Zimányi and J. Saltiel, *J. Am. Chem. Soc.*, 2000, **122**, 2377; (*j*) C. D. Berweger, W. F. van Gunsteren and F. Müller-Plathe, *Angew. Chem., Int. Ed.*, 1999, **38**, 2609; (*k*) M. G. Steinmetz, C. Luo and G. Liu, *J. Org. Chem.*, 1999, **64**, 2057; (*l*) G. Liu, L. Heisler, L. Li and M. G. Steinmetz, *J. Am. Chem. Soc.*, 1996, **118**, 11412; (*m*) H. Meier, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1399; (*n*) D. H. Waldeck, *Chem. Rev.*, 1991, **91**, 415.

12 (*a*) M. Y. Paik, S. Krishnan, F. You, X. Li, A. Hexemer, Y. Ando, S. H. Kang, D. A. Fischer, E. J. Kramer and C. K. Ober, *Langmuir*, 2007, **23**, 5110; (*b*) C.-S. Tsai, J.-K. Wang, R. T. Skodje and J.-C. Lin, *J. Am. Chem. Soc.*, 2005, **127**, 10788; (*c*) Y. Wen, W. Yi, L. Meng, M. Feng, G. Jiang, W. Yuan, Y. Zhang, H. Gao, L. Jiang and Y. Song, *J. Phys. Chem. B*, 2005, **109**, 14465; (*d*) C. T. Konek, K. D. Illg, H. A. Al-Abadleh, A. B. Voges, G. Yin, M. J. Musorrafiti, C. M. Schmidt and F. M. Geiger, *J. Am. Chem. Soc.*, 2005, **127**, 15771; (*e*) G. J. Ashwell and A. Mohib, *J. Am. Chem. Soc.*, 2005, **127**, 16238; (*f*) T. Nakabayashi, M. Wahadoszamen and N. Ohta, *J. Am. Chem. Soc.*, 2005, **127**, 7041; (*g*) N. Delorme, J.-F. Bardeau, A. Bulou and F. Poncin-Epaillard, *Langmuir*, 2005, **21**, 12278; (*h*) A. D. Shukla, D. Strawser, A. C. B. Lucassen, D. Freeman, H. Cohen, D. A. Jose, A. Das, G. Evmenenko, P. Dutta and M. E. van der Boom, *J. Phys. Chem. B*, 2004, **108**, 17505; (*i*) D. Witt, R. Klajn, P. Barski and B. A. Grzybowski, *Curr. Org. Chem.*, 2004, **8**, 1763; (*j*) X. Zhan, S. Wang, Y. Liu, X. Wu and D. Zhu, *Chem. Mater.*, 2003, **15**, 1963; (*k*) J. Zhang, J. K. Whitesell and M. A. Fox, *J. Phys. Chem. B*, 2003, **107**, 6051; (*l*) J. Hu, J. Zhang, F. Liu, K. Kittredge, J. K. Whitesell and M. A. Fox, *J. Am. Chem. Soc.*, 2001, **123**, 1464; (*m*) J. Zhang, J. K. Whitesell and M. A. Fox, *Chem. Mater.*, 2001, **13**, 2323; (*n*) G. Klärner, J.-lk. Lee, M. H. Davey and R. D. Miller, *Adv. Mater.*, 1999, **11**, 115; (*o*) S. D. Evans, R. S. Johnson, H. Ringsdorf, L. M. Williams and H. Wolf, *Langmuir*, 1998, **14**, 6436; (*p*) M. O. Wolf and M. A. Fox, *Langmuir*, 1996, **12**, 955; (*q*) M. O. Wolf and M. A. Fox, *J. Am. Chem. Soc.*, 1995, **117**, 1845.

13 R. Capelli, M. A. Loi, C. Taliani, H. B. Hansen, M. Murgia, G. Ruani, M. Muccini, P. W. Lovenich and W. J. Feast, *Synth. Met.*, 2003, **139**, 909.

14 M. Halim, J. N. G. Oillow, I. D. W. Samuel and P. L. Burn, *Adv. Mater.*, 1999, **11**, 371.

15 H. C. Geiger, J. Perlstein, R. J. Lachicotte, K. Wyrozebski and D. G. Whitten, *Langmuir*, 1999, **15**, 5606.

16 (*a*) G. G. Condorelli, A. Motta, M. Favazza, P. Nativo, I. L. Fragalà and D. Gatteschi, *Chem.–Eur. J.*, 2006, **12**, 3558; (*b*) G. G. Condorelli, A. Motta, I. L. Fragalà, F. Giannazzo, V. Raineri, A. Caneschi and D. Gatteschi, *Angew. Chem., Int. Ed.*, 2004, **43**, 4081.

17 A. Facchetti, L. Beverina, M. E. van der Boom, P. Dutta, G. Evmenenko, A. D. Shukla, C. E. Stern, G. A. Pagani and T. J. Marks, *J. Am. Chem. Soc.*, 2006, **128**, 2142, and references therein.

18 N. Dam, R. D. Scurlock, B. Wang, L. Ma, M. Sundahl and P. R. Ogilby, *Chem. Mater.*, 1999, **11**, 1302.

19 R. Yerushalmi, A. Scherz and M. E. van der Boom, *J. Am. Chem. Soc.*, 2004, **126**, 2700.

20 M. Repoux, *Surf. Interface Anal.*, 1992, **18**, 567.

21 D. Briggs, in *Practical Surfaces Analysis*, ed. D. Briggs and M. P. Seah, WILEY-VCH, Weinheim, Germany, 2nd edn, 1995, vol. 1, p. 183 (ch. 4.5.2) and p. 248 (ch. 5.4.3).

22 D. M. Sarno, L. J. Matienzo and W. E. Jones Jr, *Inorg. Chem.*, 2001, **40**, 6308.

23 (*a*) B. Bartlett, J. M. Valdisera and J. N. Russell Jr., *Surf. Sci.*, 1999, **442**, 265; (*b*) J. G. Serafin and C. M. Friend, *J. Am. Chem. Soc.*, 1989, **111**, 4233; (*c*) G. Beason, D. Briggs, in *High Resolution XPS of Organic Polymers: the Scienta ESCA 300 database*, John Wiley and Sons, Chichester, England, 1992, ch. 15, p. 186.

24 X. N. Xie, H. J. Chung, C. H. Sow and A. T. S. Wee, *Mater. Sci. Eng., R*, 2006, **54**, 1–48.