A Novel Route to Efficient Inorganic Oxide Surface Modifications: Molecularly Self-assembled Linear and Conjugated Alkynyl Thin Film Materials

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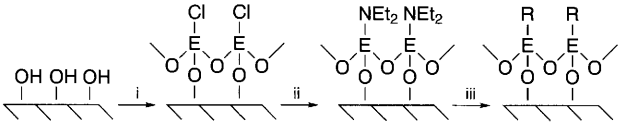
Treatment of surface hydroxy groups on glass, quartz and single crystal silicon with commercially available group 14 chlorides, ECl_4 (E = Si, Sn), and then NEt_2H yields surface-anchored NEt_2 moieties, which react with several organic molecules containing terminal acidic protons, including rigid-rod alkynes, *via* acid–base hydrolysis, leading to molecularly self-assembled chromophoric monolayers.

We report here: (i) a new, general and convenient route, based on acid–base hydrolysis, to the functionalization of inorganic oxide surfaces of glass, quartz and single crystal silicon, with a variety of chromophores; and (ii) the first examples of molecular self-assembly of rigid-rod alkynes with extended π-conjugation. The robust and highly ordered two-dimensional thin film assemblies incorporating chromophores of a diverse nature represent materials with potential applications in areas such as photonics, sensors and heterogenized homogeneous catalysis. Manipulating the cooperative forces which cause molecular self-assembly and dictate the spatial and energetic aspects in the resulting thin films is a challenging task. Fabrication of ultrathin films on solid substrates *via* molecular self-assembly requires molecules with suitable end groups to effect surface anchoring by covalent bond formation.[1] However, difficulties exist in synthesizing designed chromophores with appropriate reactive end-group functionalities. Modification of surfaces by the reaction of surface-anchored aminosilanes and -stannanes with organic chromophores containing terminal acidic protons, reported here, is a simple and versatile approach to molecular self-assembly.

The chemistry of organosilicon– and organotin–nitrogen ($Me_3E{-}NR'_2$, E = Si, Sn; R′ = Me, Et) compounds towards hydrolysis has been well documented.[2,3] Because of its lower metal-to-nitrogen bond strength, and the higher basicity of nitrogen in stannylamines than the corresponding aminosilanes, the Sn–N bond can be easily cleaved by protic species. The formation of Si–N bonds is extremely facile. The reaction of $Me_3Si{-}Cl$ in diethyl ether with excess diethylamine at room temperature gave $NEt_2H{\cdot}HCl$ and $Me_3Si{-}NEt_2$. The latter reacted with 1 mol equiv. of RH (RH = $C_6H_5{-}OH$, $C_6H_5{-}SH$, $C_6H_5{-}CO_2H$) yielding the corresponding $Me_3Si{-}R$ compounds almost quantitatively.† The compound $Me_3Sn{-}Cl$ reacted[4] with NEt_2H and RH in diethyl ether to give $Me_3Sn{-}R$† and $NEt_2H{\cdot}HCl$. We were intrigued by the behaviour of the surface-immobilized NEt_2 moiety towards organic acids leading to surface modifications based on simple acid–base hydrolysis.

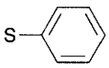
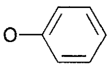
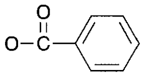
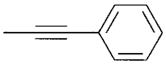
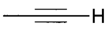
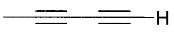
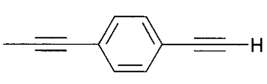
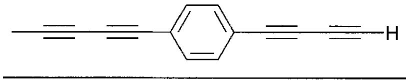
The general synthetic strategy (Scheme 1) involves the treatment of clean glass, quartz and single crystal silicon substrates‡ with: i, ECl_4 (E = Si, Sn; 10% solution by volume in toluene); ii, dry NEt_2H (5% solution by volume in toluene), followed by: iii, organic molecules containing acidic protons (R–H), leading to covalent anchoring of the conjugate base to the substrates and elimination of NEt_2H. Evolution of the monolayer structures was monitored by contact angle measurements, UV–VIS absorption, FT-Raman and XPS. The wetting characteristics of thin films were analysed by measuring static contact angles of deionized water on monolayer surfaces.§ The data presented in Table 1 is consistent with surface wettabilities:[1] clean glass surface, 18°; and E–R, 88–90°. The lower contact angles of water on these phenyl or acetylene terminated surfaces than the corresponding long alkyl chains (paraffins, *ca.* 100°) may be caused by the fact that CH groups (sp character) adhere more strongly to water than CH_3 (sp^3) groups. It has been suggested[5] that in paraffin films, the hydrogen atoms form a protective coating preventing attractive forces in a highly polar inorganic oxide surface from contributing to the spread of water drops.



Scheme 1 *Reagents and conditions*: i, ECl_4 (E = Si, Sn), toluene, room temp., 18 h; ii, NEt_2H, toluene, 70 °C, 14 h; iii, RH, toluene, 70 °C, 18 h. For E = Si, Sn: R = $S{-}C_6H_5$, $O{-}C_6H_5$, $O{-}C(O){-}C_6H_5$, $S{-}(CH_2)_n{-}Me$, $C{\equiv}C{-}C_6H_5$. For E = Sn: R = PPh_2, $C{\equiv}C{-}H$, $C{\equiv}C{-}C{\equiv}C{-}H$, $C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}H$, $C{\equiv}C{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}C{\equiv}C{-}H$.

The UV–VIS absorption spectrum of a monolayer prepared from $H{-}C{\equiv}C{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}C{\equiv}C{-}H$ on quartz, and its solution spectrum in dichloromethane are shown in Fig. 1. The two spectra are similar but the surface spectrum is broadened. The spectral absorptions at 310 and 326 nm are consistent with the solution absorptions at 302 and 322 nm. An estimation of the surface density in a monolayer of $-(Si){-}O{-}(Sn){-}C{\equiv}C{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}C{\equiv}C{-}H$ was made based on the solution absorption spectra¶ of $H{-}C{\equiv}C{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}C{\equiv}C{-}H$ and the Beer–Lambert law.[6] Using the extinction coefficient of $H{-}C{\equiv}C{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}C{\equiv}C{-}H$ (λ_{max} = 322 nm, $\varepsilon_{322} = 2.16 \times 10^7$ $dm^3\ mol^{-1}\ cm^{-1}$), the surface coverage was calculated to be 2×10^{-9} mol cm^{-2}. The latter is comparable to the reported values for surface silanol sites on acid-washed silica.[6b]

Table 1 Static contact angle (θ/°) data using water as wetting liquid for monolayers (Scheme 1) on glass. Clean glass slide with surface –OH groups: contact angle 18°

R group on the substrate	E = Si (θ/°) ± 2	E = Sn (θ/°) ± 2
	90	90
	90	88
	88	88
	86	86
		88
		88
		83
		86

Raman spectroscopy is a useful technique for probing the surface and interfacial structures in thin organic films.[1] However, because of its low detection sensitivities, reports characterizing monolayer structures using unenhanced Raman spectroscopy are scarce.[7] We were intrigued by the possibility of monitoring the evolution of the local molecular structure in monolayers using FT–Raman microspectroscopy. It was hoped that, during step-by-step construction of monolayers of organic chromophores in the direction of polarization, generation of local symmetry would lead to informative Raman spectral lines. The FT–Raman microspectra‖ from 700 to 1500 cm^{-1}, of (*a*) a clean glass slide, and monolayers of (*b*) $-(Si)-O-(Sn)-Cl$, (*c*) $-(Si)-O-(Sn)-NEt_2$, and (*d*) $-(Si)-O-(Sn)-C\equiv C-C\equiv C-C_6H_4-C\equiv C-C\equiv C-H$ on glass, are shown in Fig. 2(a). The observed spectra are consistent with the build-up of surface structure $-(Si)-O-(Sn)-C\equiv C-C\equiv C-C_6H_4-C\equiv C-C\equiv C-H$. The clean glass slide does not show any spectral features. As the monolayer structure is constructed, the band at 1090 cm^{-1} assigned to Si–O vibrations starts to increase in intensity and is clearly observed in the final monolayer structure as a sharp band. The FT–Raman spectra,** in the solid state, of (*a*) $Me_3Sn-C\equiv C-C\equiv C-C_6H_4-C\equiv C-C\equiv C-SnMe_3$, (*b*) $H-C\equiv C-C\equiv C-C_6H_4-C\equiv C-C\equiv C-H$, and (*c*) the FT–Raman microspectrum of a monolayer of $-(Si)-O-(Sn)-C\equiv C-C\equiv C-C_6H_4-C\equiv C-C\equiv C-H$ on glass, in the $C\equiv C$ stretching frequency region, are shown in Fig. 2(b). The compound $Me_3Sn-C\equiv C-C\equiv C-C_6H_4-C\equiv C-C\equiv C-SnMe_3$ (*a*) shows a sharp band at 2195 cm^{-1} which, as expected, is shifted to higher wavenumbers (2206 cm^{-1}) in $H-C\equiv C-C\equiv C-C_6H_4-C\equiv C-C\equiv C-H$ (*b*). The FT–Raman microspectrum of the monolayer (*c*) shows two overlapping peaks (2185, 2212 cm^{-1}) which are comparable in shape and position to those in the powders.

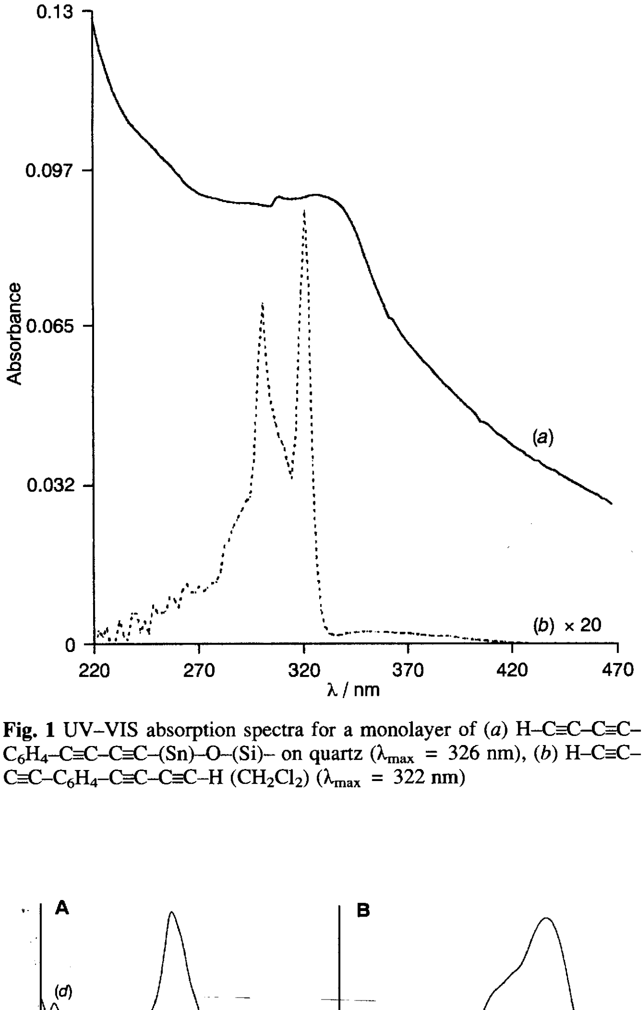


Fig. 1 UV–VIS absorption spectra for a monolayer of (*a*) $H-C\equiv C-C\equiv C-C_6H_4-C\equiv C-C\equiv C-(Sn)-O-(Si)-$ on quartz (λ_{max} = 326 nm), (*b*) $H-C\equiv C-C\equiv C-C_6H_4-C\equiv C-C\equiv C-H$ (CH_2Cl_2) (λ_{max} = 322 nm)

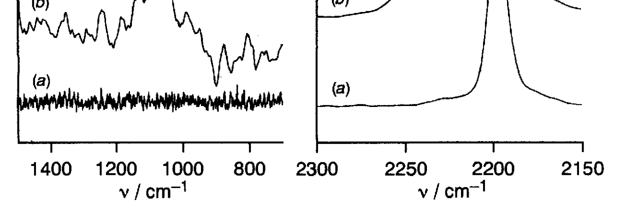


Fig. 2(A) FT–Raman microspectra (700–1500 cm^{-1}) of (*a*) clean glass slide; (*b*) glass slide functionalized with $-(Si)-O-(Sn)-Cl$ (step i, Scheme 1); (*c*) glass slide functionalized with $-(Si)-O-(Sn)-NEt_2$ (step ii, Scheme 1); and (*d*) glass slide functionalized with $-(Si)-O-(Sn)-C\equiv C-C\equiv C-C_6H_4-C\equiv C-C\equiv C-H$ (step iii, Scheme 1). (**B**): FT–Raman spectra (2150–2300 cm^{-1}) of (*a*) $Me_3Sn-C\equiv C-C\equiv C-C_6H_4-C\equiv C-C\equiv C-SnMe_3$, (*b*) $H-C\equiv C-C\equiv C-C_6H_4-C\equiv C-C\equiv C-H$; and (*c*) FT–Raman microspectrum of a monolayer of $-(Si)-O-(Sn)-C\equiv C-C\equiv C-C_6H_4-C\equiv C-C\equiv C-H$ on glass.

An analysis of the X-ray photoelectron spectrum of a monolayer of $-(Si)-O-(Sn)-C\equiv C-C\equiv C-C_6H_4-C\equiv C-C\equiv C-H$ on quartz showed the presence of Si (2p, 103.4 eV), C (1s, 284.9 eV) Sn (3d, 486.7 and 495.1 eV) and O (1s, 532.6 eV) peaks. These results, together with the data presented above, suggest that the new self-assembly technique discussed here is capable of producing stable, densely packed and organized thin films.

It has been well established that suitably oriented functionalized chromophores in ordered thin films can be subjected to topochemical polymerization.[8,9] We attempted the surface polymerization in monolayers built from $H-C\equiv C-C\equiv C-H$ and $H-C\equiv C-C\equiv C-C_6H_4-C\equiv C-C\equiv C-H$ chromophores by exposing them to UV light. Our preliminary results, based on absorption spectra, indicate that the latter monolayers can be polymerized with the subsequent formation of a blue film. Intriguingly, no detectable changes in the aqueous contact angles were observed before or after polymerization.

In conclusion, the acid–base hydrolysis of surface bound silyl- or stannyl-amines, obtained using commercially available reagents, is a general and promising approach to the functionalization of inorganic oxide surfaces. The results indicate that the rigid-rod alkynes with extended π-conjugation form stable and uniform monolayers *via* noncovalent π–π interactions. A detailed investigation of the structural and physical properties of these alkynyl surfaces, and further synthetic elaboration to multilayered structures, are currently being pursued. The surface bound NEt_2 and PPh_2 donor ligands are also very good candidates for tethering transition metal fragments leading to the formation of organometallic surfaces[10] for heterogenized homogeneous catalysis.

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Footnotes

† Characterized by NMR and MS. *Selected data*: Me_3SiNEt_2: ^1H NMR (270 MHz, C_6D_6) δ 0.25 [s, $(CH_3)_3Si$], 1.55 (t, *J* 7 Hz, 3H, CH_3), 3.27 (q, *J* 7 Hz, 2H, CH_2). $C_6H_5-CO(O)-SiMe_3$: ^1H NMR (270 MHz, C_6D_6) δ 0.57 (s,

CH_3), 7.61, 8.23 (m, C_6H_5), MS (CI) 196. C_6H_5–C≡C–$SnMe_3$: ^{1}H NMR (270 MHz, C_6D_6) δ 0.17 (s, CH_3), 6.92, 7.52 (m, C_6H_5); MS (CI) 266.

‡ The substrates were cleaned by (i) soaking in soap solution and sonocating for 30 min; (ii) washing with deionized water; (iii) treating with piranha solution (70% H_2SO_4, 30% H_2O_2) at 100 °C for 1 h [CAUTION: The piranha solution is highly potent and explosive. Proper care should be taken while using this mixture]; (iv) washing copiously with deionized water; and (v) drying with a stream of nitrogen before taking them into a nitrogen dry box.

§ The static and advancing contact angles were measured with a Rame-Hart NRL 100 goniometer. On average, 8 drops of water were measured on different areas of both sides of a glass slide for each sample, and the values reported in Table 1 are the mean values. The advancing contact angles were found to be very similar to the static values.

¶ UV-VIS CH_2Cl_2 λ_{max}/nm 322 (A 0.864); monolayer (Quartz) λ_{max}/nm 326 (A 0.0924). The spectra were collected from a quartz slide functionalized on both sides. Therefore, for calculating surface coverage, absorbance was divided by 2 to obtain the value for each individual monolayer.

‖ The FT–Raman microscopic studies were performed on a Nikon Optiphot-2 microscope connected to the FRA-106 Raman module by two 1 m optical fibres. The FRA-106 module was interfaced to a Bruker IFS-88 spectrometer. For further details of the experimental setup, see: R.D. Markwell, I. S. Butler, J. P. Gao and A. S. Shaver, *J. Raman Spectra.*, 1993, **24**, 423.

** The FT–Raman spectra were recorded on a Bruker IFS-88 spectrometer with the aid of a Bruker FRA-106 Raman module equipped with an air-cooled, 300 mW Nd : YAG laser.

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