

Synthesis and photodimerization in self-assembled monolayers of 7-(8-trimethoxysilyloctyloxy)coumarin

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We report a synthesis of 7-(8-trimethoxysilyloctyloxy)coumarin that can self-assemble into optically active monolayers on substrates. Atomic force microscopy and UV–vis spectroscopy have been used to characterize the self-assembly processes and photochemical reaction of the coumarin silane on substrates. We also show that when irradiated with linearly polarized UV light, the self-assembled coumarin monolayer can induce a homogeneous alignment of nematic liquid crystals.

Introduction

Self-assembly of appropriately functionalized molecules from a solution on a solid substrate provides a new route in creating well-defined organic surfaces.¹ Alkylsilanes are particularly of interest for surface modification strategies because they can form physically robust two-dimensional arrays on a wide range of substrates through self-assembly.² In self-assembled monolayers (SAMs), the nature of the terminal groups on the silane molecules imparts the desired surface properties. By proper choice of the functionality, it is possible to tailor surface properties and design functional thin film materials at the molecular level. Recently, much work has focused on the synthesis of functionalized alkylsilanes and the investigation of SAMs obtained from these molecules on substrates.^{3–7}

The photophysical and photochemical behavior of coumarin and its derivatives has been known for over a century. In 1902, Ciamician and Silber⁸ showed for the first time that coumarin can undergo photodimerization upon irradiation with wavelengths longer than 300 nm in ethanol. Since then, the photodimerization of coumarin has attracted considerable interest and has been studied extensively in solutions,^{9,10} crystals^{11,12} and polymer films.^{13–16} It has also been shown that coumarin can form four possible types of photodimers: *syn* head-to-head, *syn* head-to-tail, *anti* head-to-head, and *anti* head-to-tail through a [2+2] photocycloaddition. The photodimerization of coumarin is a reversible reaction. The photodimers can be cleaved to the starting coumarin upon irradiation at wavelengths shorter than 300 nm.¹⁷

SAMs presenting coumarin groups are promising candidates for constructing photoactive surfaces and photomemory thin film materials. Fox and coworkers¹⁸ reported a SAM made from coumarin-functionalized thiols on gold and showed that the reverse photochemical reactions of coumarin groups can occur in the two-dimensional monolayers. Recently, we have conducted a similar study of SAMs of coumarin-functionalized silanes. These silane molecules can form closely packed monolayers on a wide range of substrates. In this paper, we report the synthesis and self-assembly of 7-(8-trimethoxysilyloctyloxy)coumarin and describe the alignment of nematic liquid crystals on the self-assembled coumarin monolayers.

Experimental

Synthesis

The new material was prepared by the route shown in Fig. 1. The reactions were monitored and characterized by 300 MHz ¹H NMR spectra (General Electric QE300 spectrometer), infrared spectra (FT Perkin Elmer 1800 spectrophotometer), and analytical TLC (Whatman precoated silica gel 60-F254 plates).

7-(Oct-7-enyloxy)coumarin (1). In a nitrogen-flushed flask, 7-hydroxycoumarin (2.0 g, 12.3 mmol), potassium carbonate

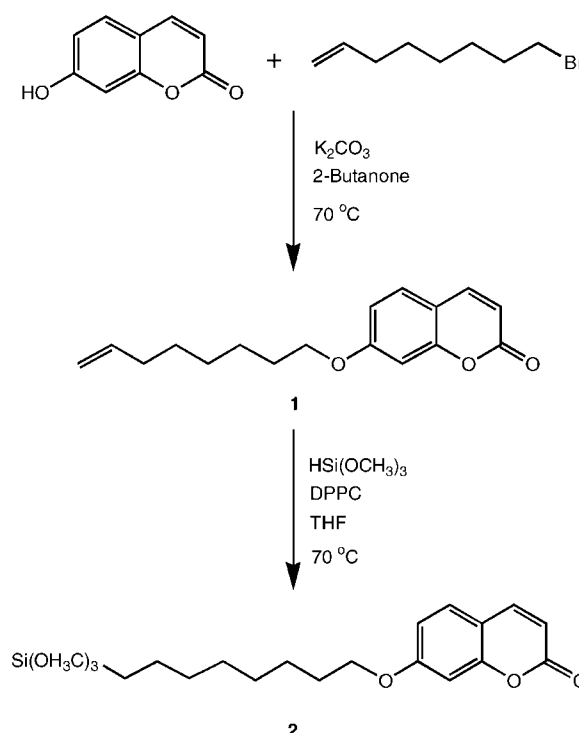


Fig. 1 Synthetic route to 7-(8-trimethoxysilyloctyloxy)coumarin.

(5.0 g, 36 mmol), and bromooctene (2.5 mL, d 1.139, 14.9 mmol) were dissolved in 50 mL butanone and heated at 70 °C for 72 hours. The solution was diluted with 25 mL water, then acidified with 1 M HCl. The aqueous layer was extracted with 2 × 50 mL portions of dichloromethane and the organic layers were isolated, dried over MgSO₄ and the solvent removed by rotatory evaporation. The residue was purified using column chromatography (silica gel, dichloromethane) to give the product as a white solid (3.1 g, 11.3 mmol, 92% yield). ¹³C NMR (CDCl₃, TMS) δ 25.8, 28.9, 29.0, 33.8, 68.7, 77.4, 101.4, 113.0, 113.1, 114.5, 128.8, 139.0, 143.5, 156.0, 162.0, 162.5. ¹H NMR (CDCl₃, TMS) δ 1.4 (m, 6 H, CH₂-CH₂), 1.7 (m, 2 H, CH₂-CH₂), 2.0 (m, 2 H, CH₂-C=C), 3.9 (t, 2 H, CH₂-O), 4.9 (m, 2 H, CH₂=CH), 5.7 (m, 1 H, CH=CH₂), 6.2 (d, 1 H, CH=CH), 6.7 (m, 2 H, ArH), 7.3 (d, 1 H, ArH), 7.6 (d, 1 H, ArH). IR (KBr pellet) 1715 (C=O), 1600 (C=C) cm⁻¹. Anal. Calcd for C₁₇H₂₀O₃: C, 74.97; H, 7.40. Found: C, 74.93; H, 7.42%. Melting point was 42–43 °C.

7-(8-Trimethoxysilyloxy)coumarin (2). The 7-(octenyl-oxy)coumarin (1) (3.1 g, 11.3 mmol) was dissolved in 15 mL of THF, then trimethoxysilane (2.5 mL, d 0.960, 19.7 mmol) and 10 mg of dicyclopentadienylplatinum(II) chloride (DPPC) catalyst were added. The mixture was stirred at 70 °C for 24 hours under nitrogen. The solvent was removed by rotatory evaporation and the residual material purified using column chromatography (silica gel, dichloromethane). The silane coumarin was isolated as a colorless liquid (0.6 g, 1.5 mmol, 26% yield). ¹³C NMR (CDCl₃, TMS) δ 9.2, 22.7, 26.0, 29.0, 29.3, 33.1, 50.6, 68.7, 77.8, 101.4, 113.0, 113.1, 128.8, 143.5, 156.0, 162.0, 162.5. ¹H NMR (CDCl₃, TMS) δ 0.6 (t, 2 H, CH₂-Si(OMe)₃), 1.8 (m, 8 H, CH₂-CH₂), 1.8 (m, 4 H, CH₂-CH₂), 3.5 (s, 9 H, Si(OCH₃)₃), 3.9 (t, 2 H, CH₂-O), 6.2 (d, 1 H, CH=CH), 6.7 (m, 2 H, ArH), 7.3 (d, 1 H, ArH), 7.6 (d, 1 H, ArH). IR (KBr pellet) 1715 (C=O), 1600 (C=C) cm⁻¹. Anal. Calcd for C₂₀H₃₀O₆Si: C, 60.89; H, 7.66; Si, 7.12. Found: C, 60.75; H, 7.61; Si, 7.10%.

Preparation of self-assembled monolayers

Silicon wafer and quartz were used as substrates. They were cleaned in 1:1 methanol–hydrochloric acid for 30 min, followed by boiling in distilled water at 100 °C for 15 minutes and drying with N₂. Self-assembled monolayers of 7-(8-trimethoxysilyloxy)coumarin were prepared by dipping these cleaned substrates in a THF solution with 1% 7-(8-trimethoxysilyloxy)coumarin for various times. The samples were then rinsed with THF and baked at 120 °C for 1 h.

Characterization of self-assembled monolayers

Contact angles of water on SAMs were measured using a goniometer (Rame-Hart, Inc.) in the ambient environment at room temperature. The precision of the contact angle measurements is $\pm 2^\circ$. UV irradiation of SAMs was conducted with a 500 W Oriel Mercury lamp equipped with monochromators and polarizers. Photodimerization of the SAMs was monitored by absorption spectra, which were recorded on a Cary 2400 spectrophotometer. A Nanoscope III atomic force microscope (Digital Instruments; Santa Barbara, CA) was used to image surface structures of SAMs. All measurements were performed in contact mode using triangle Si₃N₄ cantilevers in air under ambient conditions.

Liquid crystal cells

Two quartz plates coated with the coumarin SAMs were used to fabricate cells. The plates were mounted such that the irradiation direction in the two slides was parallel and separated by a 20 μ m Mylar spacer. Liquid crystal 5CB (4'-pentyl-4-cyanobiphenyl) was filled in the cells in the isotropic phase,

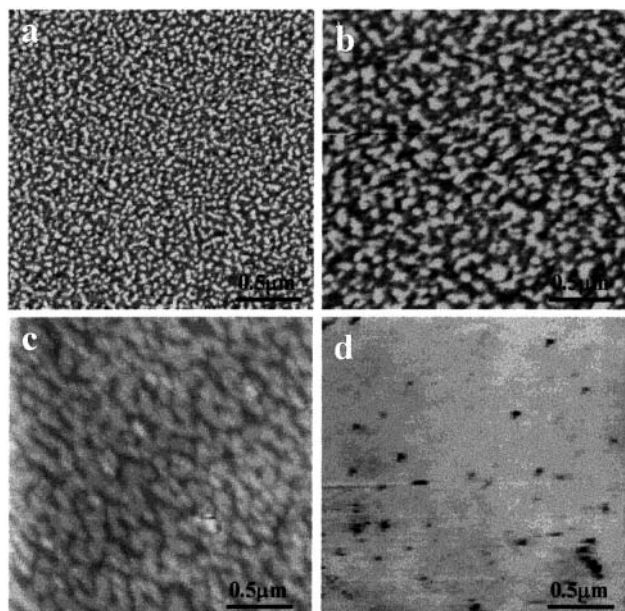


Fig. 2 Topographic AFM images of coumarin monolayer growth on a silicon wafer at different times. (a) 10 s, (b) 30 s, (c) 2 min, and (d) 5 min.

then cooled to room temperature with a gradient of 0.5 °C. An Olympus BX60 polarization microscope fitted with a photodiode was used to examine the liquid crystal alignment.

Results and discussion

Fig. 2 shows typical topographic images of the monolayer growth of 7-(8-trimethoxysilyloxy)coumarin on a silicon wafer. After 10 s, there are many islands on the surface (Fig. 2a). These islands have the same height, 1.5 ± 0.2 nm, compatible with the length of a fully extended molecule. This suggests that these islands represent a close-packed monolayer. The regions between islands represent either bare silicon or a very dilute layer of adsorbed molecules. At later times, the islands grow laterally (Fig. 2b and c), but their height remains constant. In the final stages, regions between islands fill in. The completed monolayer has a quite smooth surface, except for a few pinhole defects (Fig. 2d). The island growth is also reported in SAMs of octadecyltrichlorosilane.¹⁹

The surface coverage of the monolayer islands and contact angle of water *versus* immersion time are shown in Fig. 3. Surface coverage was calculated using the height histogram of a given image. The surface coverage correlates well with the water contact angle. The highest value of contact angle 48° was obtained for the complete monolayer.

The completed SAM was irradiated with 320 nm linearly polarized UV light. The photodimerization of coumarin groups

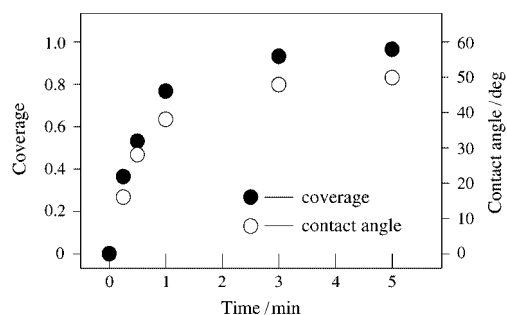


Fig. 3 Surface coverage and water contact angle *vs.* time of monolayer growth. Each data point was obtained from analyzing images from at least four widely separated locations on each sample.

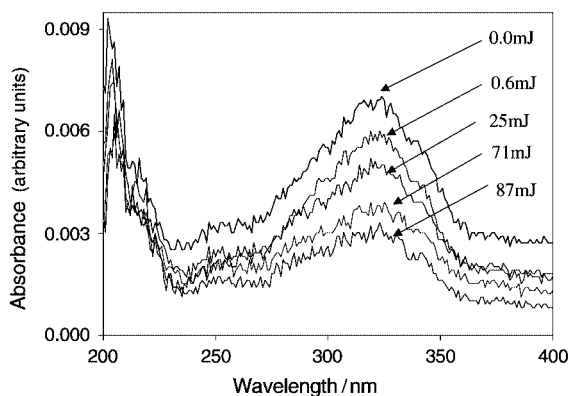


Fig. 4 Absorption spectra of coumarin SAMs irradiated with linearly polarized UV light.

in the SAM was traced by their absorption change. Before irradiation, the spectrum exhibits an absorption band at 324 nm, assigned to the absorption of the conjugated chromophore. Upon irradiation, the absorption band decreases gradually with the increase of exposure doses, as shown in Fig. 4. This decrease is attributed to the reduction in conjugation length due to the [2+2] cycloaddition. After irradiation at an exposure dose of 87 mJ cm⁻², the absorption band at 324 nm reaches a minimum. Upon further irradiation, the intensity of the absorption band remains unchanged within experimental error, suggesting that no further conversion takes place in the SAMs.

No change is observed by AFM in the topography of the irradiated SAMs. This suggests that the benzene ring systems of the cycloadducts are in the same plane as the coumarin precursors. Water contact angle on the coumarin SAMs increases from 48° to 54° after irradiation, because the cyclobutane ring on the irradiated SAM surface is less polarizable and more hydrophobic, compared to the coumarin ring at the unirradiated SAM surface. Similar changes of water contact angles on a SAM made from 7-(10-thiododecyloxy)coumarin on gold were reported by Fox and coworkers.¹⁸ They suggested that the most possible type of cyclobutane isomer is *syn* head-to-head in the irradiated SAMs.

In order to examine alignment of liquid crystals on the photodimerized SAMs, we fabricated a liquid crystal (LC) cell with the SAMs irradiated with linearly polarized light at the exposed dose of 90 mJ cm⁻². Fig. 5 shows a polarized optical microscopy image of the LC cell filled by 5CB. Under crossed polarizers, the LC cell shows a dark field with a few disclinations. The transmitted light intensity through the LC cell as a function of the rotational angle of the cell in the plane is shown in Fig. 6. The LC cell was rotated between crossed polarizer and analyser with the electric field vector of the polarized light representing the zero degree reference axes. The alternate appearance of peaks and valleys in the transmittance at every 90 degree interval shows that the transmittance is a

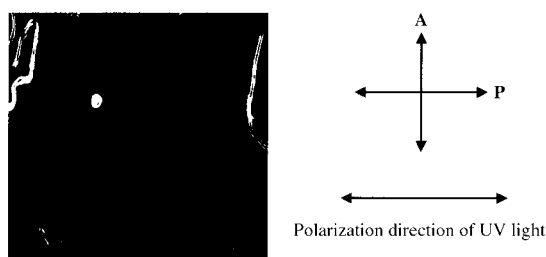


Fig. 5 Polarized optical microscopy image of a cell filled with 5CB liquid crystal. The cell was fabricated by two quartz plates coated with coumarin SAMs irradiated with linearly polarized light at the exposed dose of 90 mJ cm⁻². The image was taken under crossed polarizers.

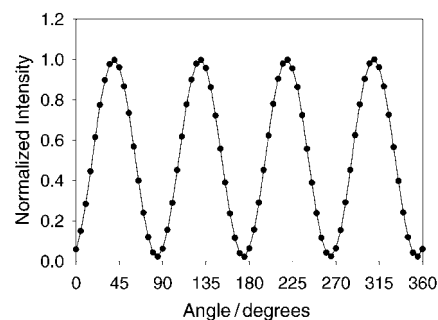


Fig. 6 Plot of the normalized intensity as a function of rotation angle of the cell between crossed polarizers.

function of $\sin^2(2\phi)$. This suggests a uniaxial alignment of 5CB molecules. The director of the nematic 5CB is parallel to the electric field vector of the incident linearly polarized light, while 5CB molecules only exhibit a parallel and isotropic alignment on the SAMs irradiated with non-polarized light at the same exposed dose.

In the case of linearly polarized UV light irradiation, only coumarin groups with a transition moment parallel to the electric field vector of the linearly polarized light dimerize favorably to form cycloadducts. The axis-selective photodimerization might lead to a preferential orientation of the phenyl rings of the cycloadducts along the direction of the exciting polarization. It is clear that the homogeneous alignment of 5CB molecules is triggered by the orientation direction of photocycloadducts generated by linearly polarized light. The alignment of nematic 5CB molecules is a result of the anisotropic interaction with the oriented cycloadducts in the SAMs. A poor alignment in nematic 5CB layers is observed for the coumarin SAMs irradiated at low exposed doses, which indicates that a certain amount of cycloadduct is required in the SAMs to create a uniform, homogeneous alignment of nematic 5CB molecules.

It has been reported by several groups that the irradiation of coumarin polymer films with linearly polarized UV light can also generate homogeneous alignment in LC layers.^{15,16} Because of the complexity of polymer films, the photoalignment mechanism is not completely understood. In addition, the alignment of LC molecules may be more or less destroyed due to the flexibility of the coumarin groups in the side chains. For example, the reversion of the LC alignment direction from parallel to perpendicular orientation was reported recently.¹⁶ In contrast to this, the SAM presenting coumarin groups provides a simple, effective alignment layer, where the coumarin groups are packed in the same plane. The density of the coumarin groups in SAMs can be controlled by mixing with non-optically active silanes. Further studies of liquid crystal alignment on mixed SAMs are under way.

Acknowledgements

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