

Microcantilever arrays functionalised with spiropyran photoactive moieties as systems to measure photo-induced surface stress changes

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Abstract

Herein we investigate the feasibility of detecting photo-induced surface stress changes using the deflection response of cantilevers. For this purpose, silicon microcantilevers have been functionalised with spiropyran photochromic molecules, using both a monolayer and a polymeric brushes approach. Upon ultraviolet light irradiation, the spiropyran unit is converted to the merocyanine form due to the photo-induced cleavage of the C_{spiro}-O bond. The two forms of the molecule have dramatically different charge, polarity and molecular conformations. This makes spiropyrans an ideal system to study the correlation between photo-induced molecular changes and corresponding changes in surface stress. Our investigations include monitoring the changes in static cantilever deflection, and consequently, surface stress of the spiropyran functionalised cantilevers on exposure to ultraviolet light. Cantilever deflection data reveals that ultraviolet induced conformational changes in the spiropyran moiety cause a change in compressive surface

stress and this varies with the type of functionalisation method implemented. The change in surface stress response from the spiropyran polymer brushes functionalised cantilevers gives an average surface stress change of 98 Nm^{-1} ($n = 8$) while the spiropyran monolayer coated cantilevers have an average surface stress change of about 446 Nm^{-1} ($n = 24$) upon irradiation with UV light.

Keywords: Microcantilever sensors, Surface stress, Nanomechanics, Molecular switch, Spiropyran, Photochromism.

1. Introduction

Cantilevers are nanomechanical transducers which produce mechanical motion arising typically from molecular interactions and over the past two decades microcantilevers have been proposed as highly versatile sensors for a wide variety of applications [1, 2]. These cantilevers are generally operated in static deflection mode, by rendering one surface sensitive to a specific external stimulus. Subsequent binding of target molecules to one side of the cantilever causes a static cantilever deflection that be correlated to a specific surface binding reaction or molecular reorganisation process. So far, microcantilever based sensors have been successfully used to monitor a variety of different physical [3, 4], chemical [5, 6] and biological interactions [7, 8]. Early work presented the silicon cantilevers for temperature sensing [4]. Further advances in nanomechanics allowed the use of microcantilevers for the detection of biomarkers and the transduction of DNA hybridisation into a nanomechanical response [9-11], along with the use of silicon cantilevers for the detection of volatile organic compounds [5]. Silicon cantilever technology also uses microcantilevers for the detection of malignant melanoma [12, 13]. Recent developments in cantilever sensor technology have demonstrated the chemo response of cantilever sensors in the detection of methane using thermally sensitive microcantilevers [14]. Other work has concentrated on improving the sensitivity of cantilever sensors by optimising the cantilever surface profile and cross-section [15]. Investigations into the performance of cantilever based sensors has reiterated the importance of the functionalisation method by comparing cantilever sensors with membrane-type surface stress sensors [16]. Cantilever sensor technology has also recently been applied in the detection of a veterinary drug kanamycin using

aptamer-based cantilever array sensors [17]. Most recently cantilevers have been used in the unique detection of organic vapours below their auto-ignition temperature using heat transfer and joule heating of the cantilevers [18].

One of the most studied photochromic systems is the inter-conversion of spiropyran (SP) to merocyanine (MC) [19-21]. Spiroprans are a class of organic molecular switches that undergo a reversible transition between a closed, non-polar and colourless SP form to a highly polar, open and coloured MC form upon irradiation with ultraviolet (UV) (365 nm) light (Figure 1). Irradiation with white light (450-550 nm) converts the MC unit back to its closed SP form [19]. The photo-conversion between these two thermodynamically stable isomeric states induce a large change in dipole moment and also surface free energy [22], making spiropyran particularly interesting targets for the development of microcantilever photo-induced surface stress sensors.

Previous work on spiropyran photochromic systems include their use for photo-induced optical sensing of metal ions, continuous flow optical sensing of solvents of different polarity [23, 24], reversible photo-actuators for microfluidic applications [25-27], photo-chemopropulsion of microdroplets [28], and self-assembly [29, 30], among others. More recently it was demonstrated that the conversion between the SP and MC form can be achieved also mechanically under tensile loading, showing the capability to create mechanochromic materials using SP containing polymers [31]. Spiropyran coated thin films have also been demonstrated by Athanassiou *et al.* as photo-actuators under UV laser irradiation due to the UV-induced conversion of SP to MC form that causes a bending in the spiropyran doped polymer film [32].

This work presents a spiropyran functionalised cantilever array implemented as a chemical sensor to detect the conformation change of the spiropyran photosensitive molecule. In this study, the dimensions of our sensor surface, in the micrometer range, are dramatically smaller than those of the system previously reported by Athanassiou *et al.* [32] permitting the use of spiropyran coated silicon microcantilevers to gain additional quantitative information on the levels of stress induced in the spiropyran film during its conformation change from the SP to the MC form (Figure 1). The merging of microcantilever technology and spiropyran photochromic molecules offers a good route for the pairing of a highly sensitive transducer with an optically controlled sensing surface.

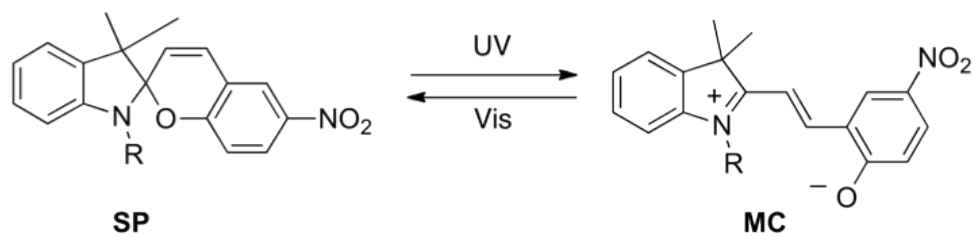


Figure 1. Photochromic behaviour of spiropyran derivatives.

2. Materials and Methods

2.1 Materials

[3-(2-Aminoethylamino)propyl]trimethoxysilane technical grade ≥ 80 (Sigma-Aldrich), 1-ethyl-3-(3dimethylamino propyl) carbodiimide hydrochloride (EDC hydrochloride) (Sigma-Aldrich), 7-Octenyltrichlorosilane (Gelest), 5-norbornene-2-carboxylic acid, *exo*- (Sigma-Aldrich), 1-(2-Hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran (SP1) (TCI Europe), *N,N'*-Dicyclohexylcarbodiimide (DCC) (Sigma-Aldrich), 4-(dimethylamino)pyridine (DMAP) (Sigma-Aldrich) and Grubbs Generation-II catalyst (Sigma-Aldrich) were used as received. 1'-(3-carboxypropyl)-3,3'-dimethyl-6-nitrospiro-1-benzopyran-2,2'-indoline (SP-COOH), was synthesised as described elsewhere [33]. The monomer (SP-norbornene) was prepared from the reaction of *exo*-5-norbornyl carboxylic acid with SP1 in the presence of *N,N'*-Dicyclohexylcarbodiimide (DCC) and 4-(Dimethylamino) pyridine (DMAP) as described elsewhere [34, 35]. For the SP-norbornene and poly (SP-norbornene) synthesis, dry tetrahydrofuran and dry dichloromethane solvents were purchased from Sigma-Aldrich and used as received. The solvents used for cleaning and solutions preparation - toluene, dichloromethane, acetone, isopropanol, ethanol and methanol reagent grade (Sigma-Aldrich), and used without further purification.

2.2 Methods

2.2.1. Cantilever Deflection Measurements

Microcantilever arrays of rectangular silicon beams with a thin layer of gold on the top side were used. Each array consists of sixteen cantilevers and four reference fixed mirrors divided in four separate wells. Cantilever arrays were fabricated from single crystal silicon and are 300 μm long, 150 μm wide, and 1 μm thick (Micromotive GmbH, Germany). The optical detection system was already described in detail by Zhang *et al.* [36]. The “optical lever” or “beam bounce” technique was implemented using a monolithic array of laser sources with an array of focusing micro-lenses and a single position sensitive optical detector (PSD). The “optical lever” technique optically records changes in the deflection of each cantilever on the array with sub-nanometer resolution. The possibility exists of using all sixteen cantilevers (four cantilevers per well) on the cantilever array simultaneously in the Veriscan set-up. Figure 2 shows a schematic of one well, containing four cantilevers and one reference rigid surface, with the laser beams reflected by the free end of each cantilever as well as the reference surface. A cantilever deflection measurement was used from each individual cantilever when the optical alignment of the laser on the back of the cantilever was optimal. If the reflected laser intensity was deemed to have not reached the minimum for accurate deflection measurements then the cantilever deflection from that cantilever was ignored. The temperature in the cell was kept constant at 23 °C.

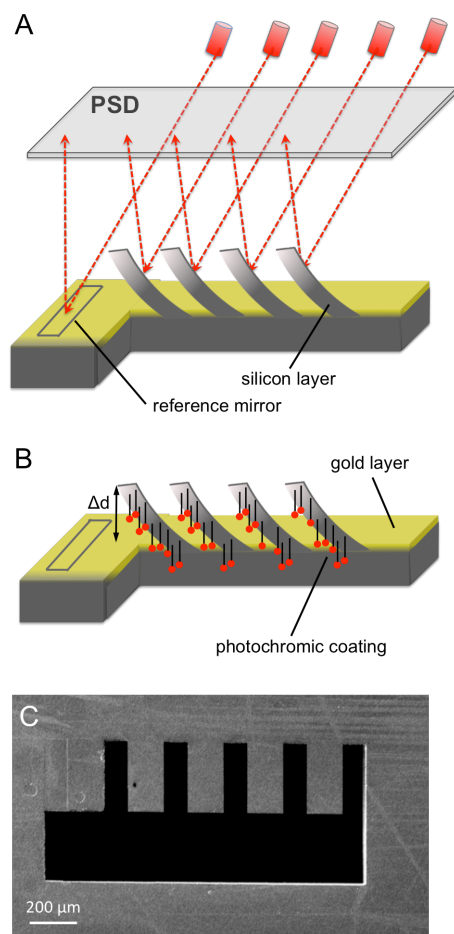


Figure 2. (a) Schematic representation of the optical deflection detection method for one of the four wells containing a cantilever array (b) cantilever bending caused by the conformation change of the photochromic layer upon exposure to UV light (c) optical image of the cantilever array and the reference rigid surface.

Two different functionalisation methods were implemented: a monolayer and a polymer brushes layer approach. Functionalised SP cantilevers were exposed to a white light LED before being placed in the system in order to ensure the full conversion of the photochromic units to the SP form. A baseline cantilever deflection was recorded before exposing the cantilevers to a UV LED. The change in the cantilever deflection response during UV exposure was monitored. The change in cantilever deflection response was recorded during exposure to UV light over a set period of time (300 s).

2.2.2 Methods of SP functionalisation

a. Functionalisation of silicon microcantilevers with spiropyran monolayers

The protocol used to coat the cantilevers with spiropyran monolayers, is described in Figure 3, steps 1–2. Prior to functionalisation, the cantilever array was washed with acetone, isopropanol, methanol and DI water, dried under a mild nitrogen stream and then treated with oxygen plasma for 2 minutes, to ensure the formation of hydroxyl groups on the silicon surface. Next, the cantilevers were coated with the spiropyran molecules using self-assembled monolayers (SAMs). The SAMs were generated by immersing the cantilever array into a 10^{-3} M solution of the silanisation agent ([3-(2-Aminoethylamino)propyl]trimethoxysilane) in toluene for 3 h at room temperature, while keeping an inert atmosphere using a glove box (Figure 3a–step 1). The amino-coated cantilevers were then cleaned with toluene to remove any unbound silanising agent, rinsed with ethanol and dichloromethane, and dried under mild nitrogen stream. The amine functionalised cantilevers were then immersed in a mixed solution of 10^{-3} M SP-COOH in ethanol, and 2×10^{-3} M EDC in water (at 1:3 proportion in volume), and left for at least 48 h at room temperature in a dark place. After that, the cantilevers were rinsed with a 1:1 methanol–water solution for 30 min to remove unbound SP-COOH molecules. Finally, they were washed with copious amounts of deionised water and dried under a mild nitrogen stream. Prior to deflection testing, all cantilevers were stored in the dark, at room temperature. A scheme of the functionalised cantilever is shown in Figure 3b.

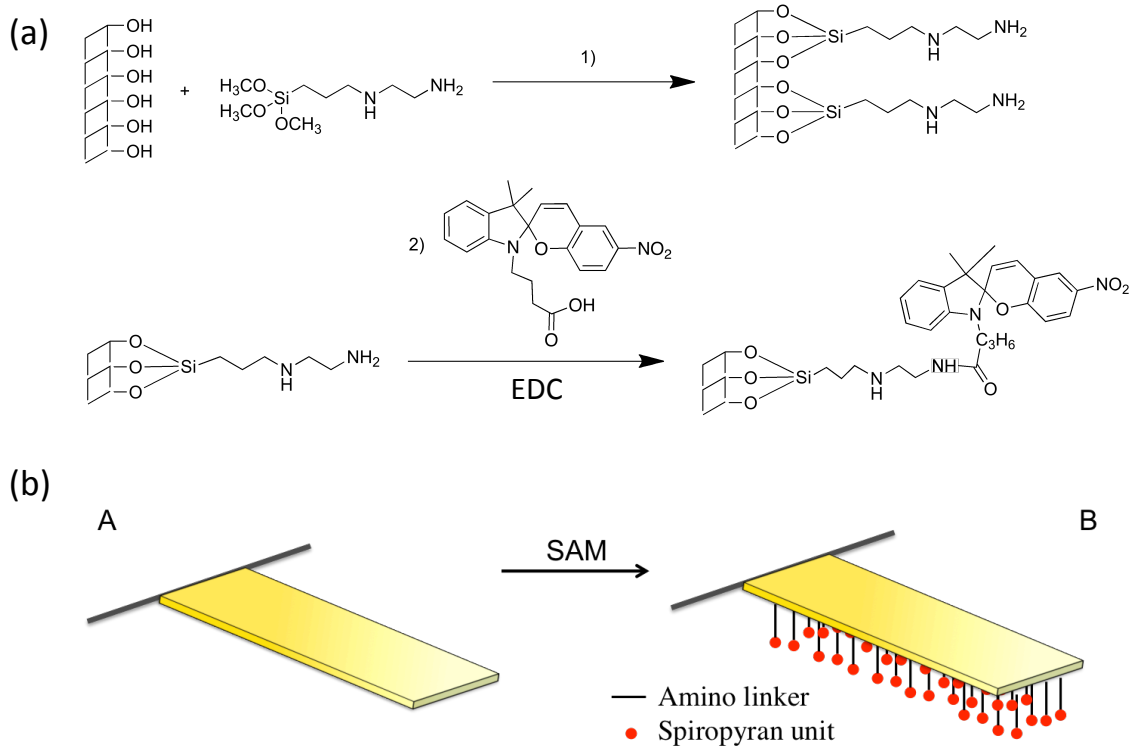


Figure 3.a) Scheme describing the functionalisation of the cantilevers with spiropyran self-assembled monolayers; b) Schematic representation of the cantilever before (A) and after functionalisation with spiropyran self-assembled monolayers (B).

b. Functionalisation of silicon microcantilevers with spiropyran polymeric brushes

The functionalisation of the cantilevers with spiropyran polymeric brushes was achieved using surface-initiated ring-opening metathesis polymerisation (Si-ROMP) as schematically described in Figure 4a, steps 1-4.

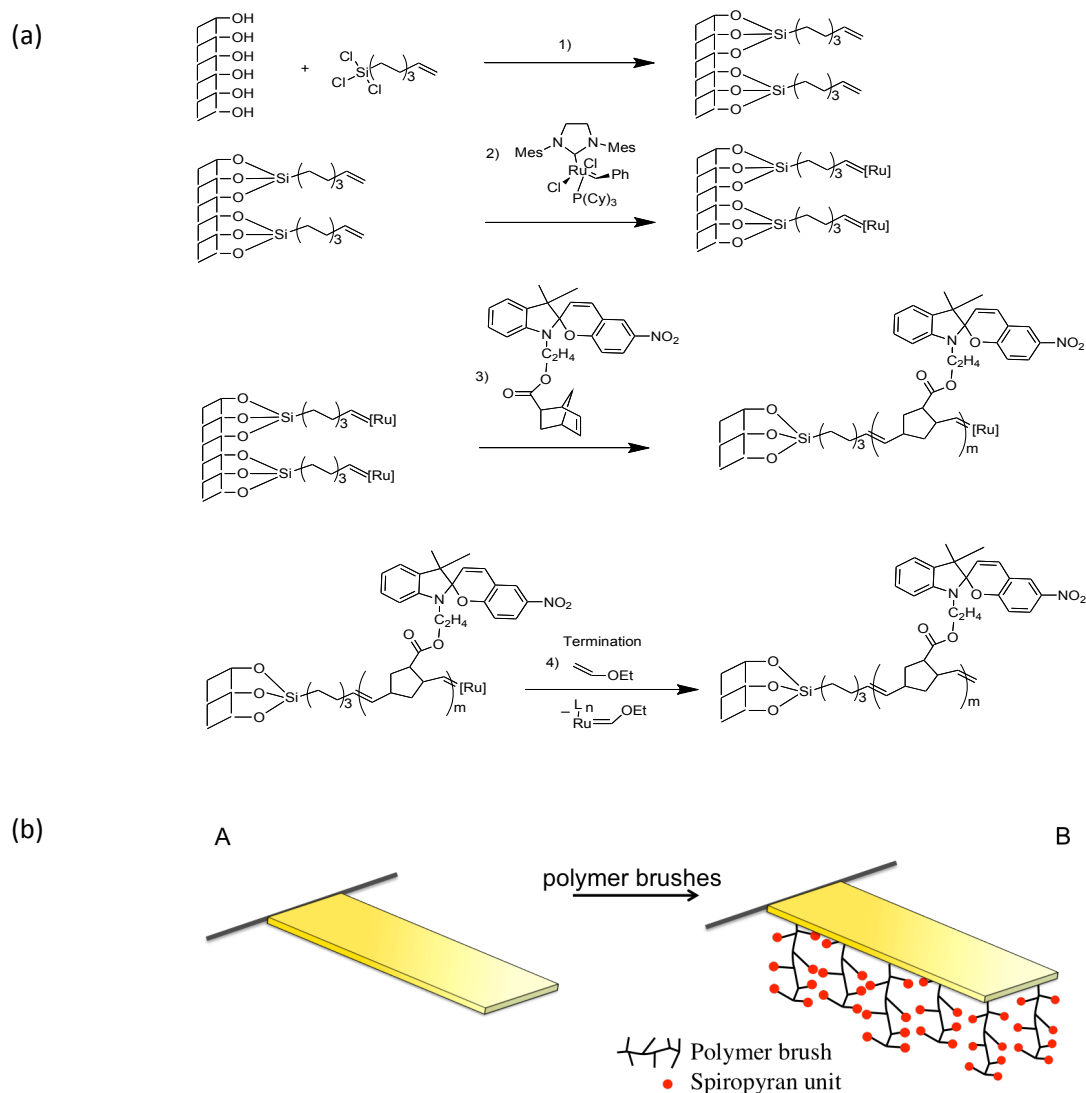


Figure 4.a) Scheme describing the functionalisation of the cantilevers with spiropyran polymeric brushes using surface-initiated ring opening metathesis polymerisation. b) representation of the cantilever before (A) and after functionalisation with spiropyran polymeric brushes using surface-initiated ring opening metathesis polymerisation (B).

Prior to functionalisation, the cantilevers were washed with acetone, water and dried under mild nitrogen stream, then treated with oxygen plasma for 2 minutes, to ensure the formation of hydroxyl groups on the silicon surface. Next, the cantilevers were immersed in a solution of the silanisation agent (7-octenyl trichlorosilane) 0.1 M in dry toluene for 90 minutes (Fig. 4–step 1). They were then washed with acetone, dried under mild nitrogen stream, and left at room temperature for 24h. Later, they were exposed to a solution of Grubbs Catalyst Second

Generation 0.02 M in degassed dichloromethane for 2 h at room temperature (Fig. 4–step 2). After, the catalyst-attached cantilever was washed several times with degassed dichloromethane. Finally, the cantilever was exposed to a solution of spiropyran functionalised monomer, 0.2 M in degassed dichloromethane, for 8 h at room temperature and inert atmosphere (Fig. 4a–step 3). Steps 2 and 3 were conducted in an inert atmosphere using a glove box. The polymerisation was quenched by adding excess of ethyl vinyl ether (Fig. 4a–step 4). Finally the array was washed with acetone to remove any physisorbed materials and left to dry. A scheme of a functionalised cantilever is shown in Fig. 4b.

2.2.3. SP Functionalised silicon substrate characterisation by Atomic Force Microscopy

Atomic Force Microscopy (AFM) characterisation was carried out using a commercial system (MFP-3D™ AFM, Asylum Research). AFM contact mode topography imaging and scratch thickness measurements of the dry SP functionalised cantilever substrates were implemented to produce surface topography scans and to determine the SP film thickness on the cantilever substrates, respectively. Scratches were produced using a scalpel for thickness measurements on the functionalised layers.

2.2.4. Calculation of surface stress

Differential stress was calculated using Equation 1 [6]

$$\Delta\sigma = \frac{Et_s}{6t_f(t_s+t_f)L} \Delta d \quad (1)$$

Where $\Delta\sigma$ is the differential stress, t_f is the SP film thickness, t_s is the substrate thickness, L is the length of the cantilever, E is the Young's modulus of the cantilever, and Δd is the measured deflection. Once the geometry and material properties of the cantilever are determined, then the cantilever displacement, Δd , is directly proportional to the change in surface stress, $\Delta\sigma$. The consequent change of the cantilever surface stress can be measured by detecting the cantilever deflection and so the chemical process occurring on the cantilever surface can be detected and

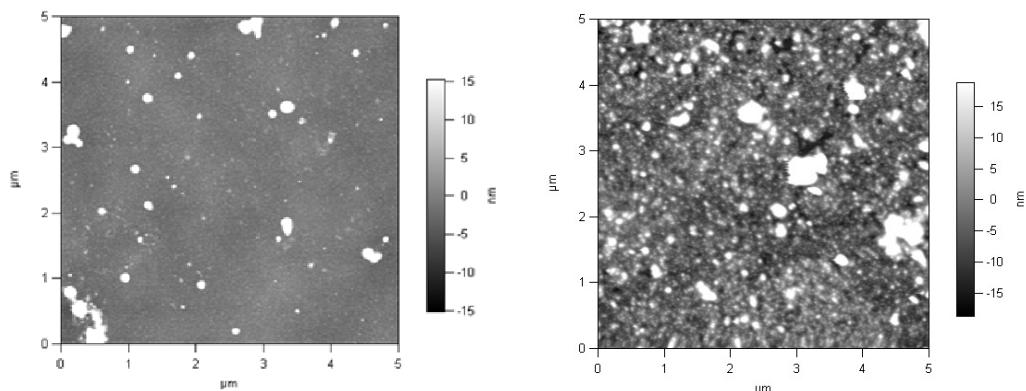
investigated. The cantilever dimensions provided by the supplier were used, assuming a Young's modulus of 180 GPa. The average cantilever deflection was calculated as the difference between the deflection of the functionalised cantilevers and the uncoated cantilever. Subtracting the spiropyran cantilever deflection from the uncoated deflection enables the response contribution due to the thermal and Schottky effects to be removed.

3. Results and Discussion

3.1. Cantilever Characterisation

Atomic Force Microscope characterisation of the spiropyran monolayer and the spiropyran polymer brushes samples was performed before UV exposure in the dry state. AFM topography scans of both coatings showed that a dense coating was produced using the ROMP polymer brushes grafting technique, and that this result is similar to the topography scans of SP polymer brushes shown by Samanta *et al.*[37] when a similar surface functionalisation technique was employed. Topography scans of the spiropyran monolayer coatings showed a less dense coating than that of the spiropyran polymeric brushes, see Figure 5(a) and (b). AFM topography scans revealed the same reproducible morphology over different cantilever substrates.

The monolayer spiropyran and the polymer brushes spiropyran film thickness was measured to be on average 8 nm +/- 3.5 nm (n = 3) and 21 nm +/- 10 nm (n = 3), respectively, using contact mode AFM scratch thickness tests mentioned earlier. The thickness of the monolayer (8 nm +/- 3.5 nm (n = 3)) was much greater than expected, ~2.5 nm as revealed using MOPAC. This could be explained from the AFM topography of SP monolayer (Figure 5a), that shows a thin homogenous coverage bellow 5nm tickness with dispersed large agglomerates (>15nm). A thicker spiropyran layer was produced, as expected, with the polymer brushes approach similar to those produced by Samanta *et al.* under similar experimental conditions [37].



(a)

(b)

Figure 5. AFM topography of SP monolayer (a) and SP polymer brushes (b) functionalised silicon substrate of cantilever array.

3.2. Photo-induced Cantilever Deflection and Surface Stress Measurements

Figure 6 presents the typical cantilever deflection response before and during UV exposure from (a) a monolayer reference cantilever, (b) a SP monolayer functionalised cantilever, (c) an uncoated polymer brush reference cantilever and (d) a SP polymer brushes cantilever. The reference SP cantilever is a cantilever with an amino-terminated silanising agent monolayer but without the spiropyran molecule. Although there is significant drift on some of the deflection data, the results show a clear difference between the cantilever deflection response from the test SP functionalised cantilevers and the reference cantilevers indicating the detection of the change of conformation of the SP molecule.

As can be seen in Table 1, the cantilever deflection response from the polymer brushes SP is less varied and smaller than the deflection response obtained from the monolayer SP functionalisation approach. The reference monolayer cantilever and the uncoated reference cantilevers all show a significantly smaller deflection response during exposure to UV light compared to the functionalised SP cantilevers. The results clearly showed that the test cantilever deflection response, due to the change in conformation of the spiropyran, is larger than the reference cantilever response. This conformational change between the SP and MC form is

expected since it was previously confirmed by UV-Vis spectroscopy when similar functionalisation procedures were used by us and others for other type of substrates such as silica microbeads [38], glass slides and glass micro-capillaries [33] (monolayer), and for glass slides [37] and glass micro-capillaries (SP brushes) [23, 24].

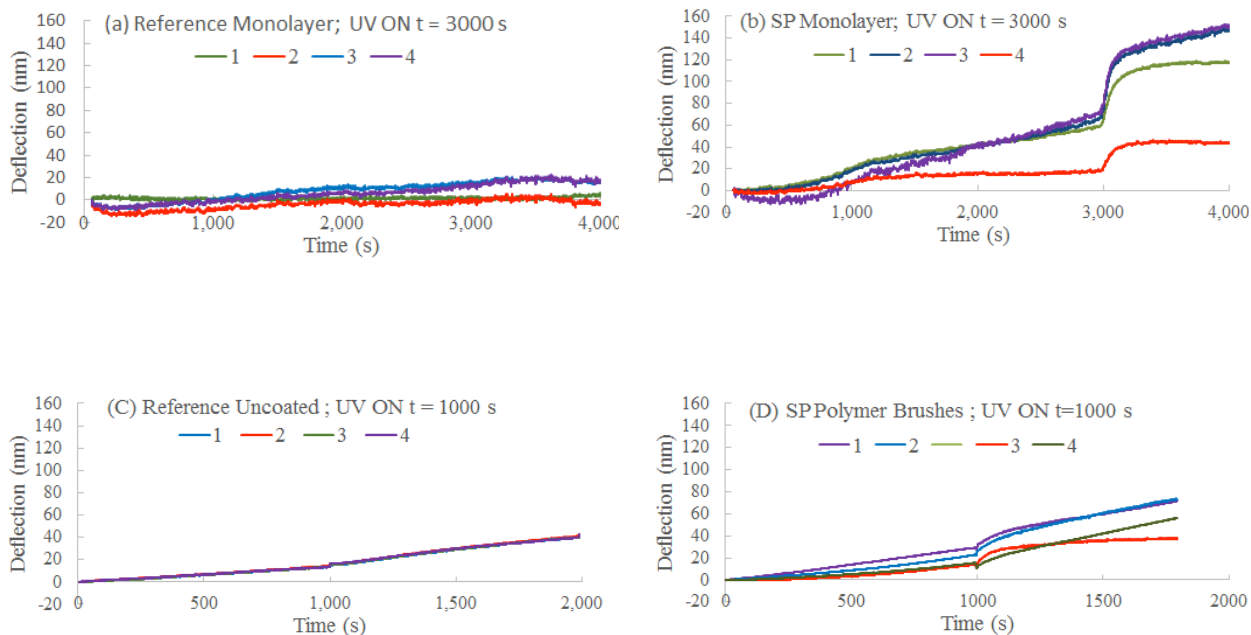


Figure 6. Example cantilever deflection responses of Reference and Test SP cantilever sensors; (a) Reference Monolayer, (b) SP Monolayer (c) Reference Uncoated and (d) SP Polymer Brushes functionalised cantilevers pre and during UV exposure.

Table 1. Cantilever deflection response on exposure to UV light.

Substrate functionalisation type	Cantilever Deflection		Number of samples (n)
	Mean (nm)	Standard Deviation (nm)	
Reference Uncoated	14	5	28
Reference Monolayer	6	0.5	6
SP Monolayer	50	26	8
SP Polymer Brushes	35	13	24

Cantilever bending is induced as a result of light irradiation by two different processes. The first and fastest bending is due to photo-induced stresses caused by charge carriers being created as a result of photons of sufficient energy promoting electrons across the Schottky barrier. The second process is due to the slow bending of the cantilever due to thermal expansion, as a result of the absorption of photons whose energy is transformed into heat and has been studied by other groups [39, 40].

As the cantilevers in these tests were exposed to light, the thermal and Schottky effect on cantilever deflection was measured. The cantilever deflection response, on exposure to UV light, for the reference uncoated cantilevers (thermal and Schottky effect) was found to be on average *ca.* 14 nm, see Table 1 above, this is within the same range as results obtained by Helm *et al.* [41] who measured the deflection due to the Schottky effect on exposure to UV light (350 nm) to be on average *ca.* 5 nm. A comparison of the thermal and Schottky effect values obtained by Helm *et al.* and this work are reasonable considering the dependence on the type of cantilever deflection systems and the used set-up. The deflection response of spiropyran functionalised cantilevers is believed to be due to a combination of the thermal effect, the Schottky effect and the spiropyran conformation change, whereas the deflection response of reference uncoated cantilevers is due to the thermal and Schottky effect solely. The cantilever deflection response for uncoated cantilevers to UV light shows the thermal and Schottky deflection response (14 nm) is well below the deflection response from the spiropyran functionalised cantilevers on exposure to UV light, which is on average 50 nm for the monolayer spiropyran functionalised cantilevers and 35 nm for the polymer brushes spiropyran functionalised cantilevers. The dominant factor causing the increased deflection response of the SP functionalised cantilevers compared to the reference cantilevers is the conformation change of SP.

The type of SP functionalisation method implemented was seen to affect the level of the cantilever deflection response on exposure to UV. The deflection response from the SP polymer brushes functionalised cantilevers is smaller compared to the SP monolayer approach and the response time is longer, as seen in Figure 6. The differences in speed of response can be attributed to the fact that the spiropyran has a greater degree of freedom required for conformation change in response to light in the monolayer approach compared to the polymeric

brushes, where due to the high density of SP units in the polymeric chain, the steric hindrance can decrease the ring-opening kinetics of the spiropyran as shown previously in the case of similar SP polymer brush coatings [23]. This would also explain the time delay in deflection response of the cantilever. Moreover, the smaller deflection response of the polymeric brushes cantilevers could be explained considering that in the polymeric brushes the SP unit appears as a pendant group in the polymeric chain, meaning that the distance from the cantilever surface to the SP unit is much greater than in the case of the monolayer, which would cause a smaller stress change on the cantilever surface, and therefore a smaller cantilever deflection. This work is validated by Wu *et al.* [42] who found that the efficiency of stress transmission dramatically decreased by increasing the chain length of linker used between the receptor molecule and the microcantilever surface.

The change in surface stress of the different cantilevers on exposure to UV light was also calculated using the measured cantilever deflection and equation (2). The surface stress was calculated using the differential cantilever deflection which is test cantilever deflection minus reference cantilever deflection. Table 2 shows the variation in surface stress compared to the functionalisation process used.

Table 2. Differential deflection and surface stress for cantilevers SP coated with the two employed processes.

	Film Thickness (nm)	SP Cantilever deflection* (nm)	Surface Stress** (N m ⁻¹)
SP Monolayer	8	36	446
SP Polymer Brushes	21	21	98

* SP Cantilever deflection minus reference cantilever deflection; **Surface Stress due to SP conformation change.

Mathad *et al.* [40] lists the three main factors which affect surface stress: surface reconstruction, intermolecular forces, and interaction energies. When the SP changes to the MC form there is a change in polarity as well as a change in the overall charge [19]. This induces a repulsive force in the functionalised layer probably due to the strong repulsion produced by the anionic nitrophenolate group of MC thus inducing a change in surface stress [43].

In both the monolayer and polymer brushes approaches it is known that the free end of the MC dipole is negative and consequently results in repulsive forces between neighbouring MC molecules. Steric effects due to the different volumes occupied by the SP and MC form also contribute to the change in surface stress of the cantilever. The MC occupies a larger volume than the SP form and consequently contributes further to the intermolecular repulsive forces arising. The change in volume in the monolayer approach is also much closer to the surface. The polymer brushes are more mobile and the change in volume of the attached MC is at a greater distance from the cantilever surface, thus contributing less to the intermolecular forces and the corresponding change in surface stress. This has been endorsed by the cantilever deflection and surface stress data that shows a smaller surface stress induced in the polymer brushes spiropyran cantilevers (*ca.* 98 N m⁻¹, Table 2) compared to the spiropyran monolayer functionalised cantilevers on exposure to UV light (*ca.* 446 N m⁻¹, Table 2). Similar surface stress values (~50 N m⁻¹) were calculated from microcantilevers, to detect changes in solvent type and pH, with end-grafted stimulus responsive polymer brushes by Abu-Lail *et al.* [6].

4. Conclusions

This work presents systematic deflection measurements of silicon microcantilevers coated with spiropyran photo-active molecules. Arrays of sixteen rectangular silicon cantilevers coated with a thin layer of gold on one side and SP moieties on the opposite side were used and their deflection response was measured during photo-activation with UV light. Different immobilisation procedures were tested based either on a monolayer approach, or on the use of grafted polymer brushes, where each monomer contains a SP unit.

Cantilevers with immobilised SP moieties produced, on exposure to UV light, a larger deflection response compared to uncoated ones. This was attributed to UV induced conformational changes of spiropyran molecules to their MC form that induce a compressive stress onto the cantilever surface, not balanced by the opposite, gold coated side. It was found that SP polymer brushes functionalisation method produced a more consistent, but smaller, change in surface stress and consequent cantilever deflection than a monolayer functionalisation approach. To conclude, a

microcantilever based device has been demonstrated which mechanically transduces conformational changes of photochromic molecules. The cantilever sensor presented here allows quantification of photo-induced molecular change occurring on the cantilever surface, demonstrating its applicability, among others, for measuring molecular changes. Future work will include investigating the reversibility of spiropyran-merocyanine isomerisation using functionalised cantilevers and the ability to detect the presence of different metal ions as the merocyanine form of spiropyran unit is well known for its binding capacity towards divalent metal ions among other charged species [44-46]. This would open the possibility of producing a chemical microsensor which can be optically turned ON/OFF.

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References

- [1] H.P. Lang, M. Hegner, C. Gerber, Cantilever array sensors, *Materials Today*, 8(2005) 30-6.
- [2] R. Raiteri, M. Grattarola, H.J. Butt, P. Skladal, Micromechanical cantilever-based biosensors, *Sensors and Actuators B-Chemical*, 79(2001) 115-26.
- [3] S. Dohn, O. Hansen, A. Boisen, Cantilever based mass sensor with hard contact readout, *Applied Physics Letters*, 88(2006) -.
- [4] T. Thundat, R.J. Warmack, G.Y. Chen, D.P. Allison, Thermal and Ambient-Induced Deflections of Scanning Force Microscope Cantilevers, *Applied Physics Letters*, 64(1994) 2894-6.
- [5] Y. Dong, W. Gao, Q. Zhou, Y. Zheng, Z. You, Characterization of the gas sensors based on polymer-coated resonant microcantilevers for the detection of volatile organic compounds, *Analytica Chimica Acta*, 671(2010) 85-91.
- [6] N.I. Abu-Lail, M. Kaholek, B. LaMattina, R.L. Clark, S. Zauscher, Micro-cantilevers with end-grafted stimulus-responsive polymer brushes for actuation and sensing, *Sensors and Actuators B-Chemical*, 114(2006) 371-8.

- [7] S. Wu, T. Nan, C. Xue, T. Cheng, H. Liu, B. Wang, et al., Mechanism and enhancement of the surface stress caused by a small-molecule antigen and antibody binding, *Biosensors and Bioelectronics*, 48(2013) 67-74.
- [8] S. Stolyarova, S. Cherian, R. Raiteri, J. Zeravik, P. Skladal, Y. Nemirowsky, Composite porous silicon-crystalline silicon cantilevers for enhanced biosensing, *Sensors and Actuators B-Chemical*, 131(2008) 509-15.
- [9] A. Boisen, T. Thundat, Design & fabrication of cantilever array biosensors, *Materials Today*, 12(2009) 32-8.
- [10] J. Fritz, M.K. Baller, H.P. Lang, H. Rothuizen, P. Vettiger, E. Meyer, et al., Translating Biomolecular Recognition into Nanomechanics, *Science*, 288(2000) 316-8.
- [11] C. Grogan, R. Raiteri, G.M. O'Connor, T.J. Glynn, V. Cunningham, M. Kane, et al., Characterisation of an antibody coated microcantilever as a potential immuno-based biosensor, *Biosensors & Bioelectronics*, 17(2002) 201-7.
- [12] F. Huber, H.P. Lang, N. Backmann, D. Rimoldi, C. Gerber, Direct detection of a BRAF mutation in total RNA from melanoma cells using cantilever arrays, *Nature Nanotechnology*, 8(2013) 125-9.
- [13] G.S. Shekhawat, V.P. Dravid, Nanomechanical Sensors Bent on Detecting Cancer, *Nature Nanotechnology*, 8(2013) 77-8.
- [14] M. Rahimi, I. Chae, J.E. Hawk, S.K. Mitra, T. Thundat, Methane sensing at room temperature using photothermal cantilever deflection spectroscopy, *Sensors and Actuators B: Chemical*, 221(2015) 564-9.
- [15] J. Zhao, Y. Zhang, R. Gao, S. Liu, A new sensitivity improving approach for mass sensors through integrated optimization of both cantilever surface profile and cross-section, *Sensors and Actuators B: Chemical*, 206(2015) 343-50.
- [16] F. Loizeau, T. Akiyama, S. Gautsch, P. Vettiger, G. Yoshikawa, N.F. De Rooij, Comparing membrane-and cantilever-based surface stress sensors for reproducibility, *Sensors and Actuators A: Physical*, 228(2015) 9-15.
- [17] X. Bai, H. Hou, B. Zhang, J. Tang, Label-free detection of kanamycin using aptamer-based cantilever array sensor, *Biosensors and Bioelectronics*, 56(2014) 112-6.
- [18] I. Jahangir, E.B. Quddus, G. Koley, Unique detection of organic vapors below their auto-ignition temperature using III-V Nitride based triangular microcantilever heater, *Sensors and Actuators B: Chemical*, 222(2016) 459-67.
- [19] L. Florea, D. Diamond, F. Benito-Lopez, Photo-Responsive Polymeric Structures Based on Spiropyran, *Macromolecular Materials and Engineering*, 297(2012) 1148-59.
- [20] S.R. Keum, M.S. Hur, P.M. Kazmaier, E. Buncel, Thermochromic and photochromic dyes - indolino-benzospiropyran .1. uv-vis spectroscopic studies of 1,3,3-spiro(2H-1-benzopyran-2,2'-indolines) and the open-chain merocyanine forms - solvatochromism and medium effects on spiro ring formation, *Can J Chem*, 69(1991) 1940-7.
- [21] S.M. Aldoshin, Spiropyran - structural features and photochemical properties, *Molecular Crystals and Liquid Crystals Science and Technology Section a-Molecular Crystals and Liquid Crystals*, 246(1994) 207-14.
- [22] N. Wagner, P. Theato, Light-induced wettability changes on polymer surfaces, *Polymer*, 55(2014) 3436-53.
- [23] L. Florea, A. McKeon, D. Diamond, F. Benito-Lopez, Spiropyran polymeric microcapillary coatings for photodetection of solvent polarity, *Langmuir*, 29(2013) 2790-7.
- [24] L. Florea, A. Hennart, D. Diamond, F. Benito-Lopez, Synthesis and characterisation of spiropyran-polymer brushes in micro-capillaries: Towards an integrated optical sensor for continuous flow analysis, *Sensors and Actuators B-Chemical*, 175(2012) 92-9.
- [25] B. Ziolkowski, L. Florea, J. Theobald, F. Benito-Lopez, D. Diamond, Self-protonating spiropyran-co-NIPAM-co-acrylic acid hydrogel photoactuators, *Soft Matter*, 9(2013) 8754-60.
- [26] J. ter Schiphorst, S. Coleman, J.E. Stumpel, A. Ben Azouz, D. Diamond, A.P. Schenning, Molecular Design of Light-Responsive Hydrogels, For in Situ Generation of Fast and Reversible Valves for Microfluidic Applications, *Chemistry of Materials*, 27(2015) 5925-31.

- [27] B. Ziółkowski, L. Florea, J. Theobald, F. Benito-Lopez, D. Diamond, Porous self-protonating spiropyran-based NIPAAm gels with improved reswelling kinetics, *Journal of Materials Science*, (2015) 1-8.
- [28] L. Florea, K. Wagner, P. Wagner, G.G. Wallace, F. Benito-Lopez, D.L. Officer, et al., Photo-Chemopropulsion–Light-Stimulated Movement of Microdroplets, *Advanced Materials*, 26(2014) 7339-45.
- [29] L. Florea, S. Scarmagnani, F. Benito-Lopez, D. Diamond, Self-assembled solvato-morphologically controlled photochromic crystals, *Chemical Communications*, 50(2014) 924-6.
- [30] Q. Chen, Y. Feng, D. Zhang, G. Zhang, Q. Fan, S. Sun, et al., Light-Triggered Self-Assembly of a Spiropyran-Functionalized Dendron into Nano-/Micrometer-Sized Particles and Photoresponsive Organogel with Switchable Fluorescence, *Advanced Functional Materials*, 20(2010) 36-42.
- [31] B.A. Beiermann, D.A. Davis, S.L.B. Kramer, J.S. Moore, N.R. Sottos, S.R. White, Environmental effects on mechanochemical activation of spiropyran in linear PMMA, *Journal of Materials Chemistry*, 21(2011) 8443-7.
- [32] A. Athanassiou, K. Lakiotaki, M. Kalyva, S. Georgiou, C. Fotakis, Photoswitches operating upon ns pulsed laser irradiation, *Applied Surface Science*, 248(2005) 56-61.
- [33] R. Rosario, D. Gust, M. Hayes, F. Jahnke, J. Springer, A.A. Garcia, Photon-modulated wettability changes on spiropyran-coated surfaces, *Langmuir*, 18(2002) 8062-9.
- [34] S.-R. Keum, S.-M. Ahn, S.-J. Roh, S.-Y. Ma, The synthesis and spectroscopic properties of novel, photochromic indolinobenzospiropyran-based homopolymers prepared via ring-opening metathesis polymerization, *Dyes Pigm.*, 86(2010) 74-80.
- [35] L. Florea, A. Hennart, D. Diamond, F. Benito-Lopez, Synthesis and characterisation of spiropyran-polymer brushes in micro-capillaries: Towards an integrated optical sensor for continuous flow analysis, *Sens Actuators B: Chem*, 175(2012) 92-9.
- [36] R. Zhang, A. Best, R. Berger, S. Cherian, S. Lorenzoni, E. Macis, et al., Multiwell micromechanical cantilever array reader for biotechnology, *Review of Scientific Instruments*, 78(2007) 084103.
- [37] S. Samanta, J. Locklin, Formation of photochromic spiropyran polymer brushes via surface-initiated, ring-opening metathesis polymerization: Reversible photocontrol of wetting behavior and solvent dependent morphology changes, *Langmuir*, 24(2008) 9558-65.
- [38] S. Scarmagnani, C. Slater, F. Benito-Lopez, D. Diamond, Z. Walsh, B. Paull, et al., Photoreversible ion-binding using spiropyran modified silica microbeads, *International Journal of Nanomanufacturing*, 5(2009) 38-52.
- [39] P.G. Datskos, T. Thundat, Nanocantilever signal transduction by electron transfer, *Journal of Nanoscience and Nanotechnology*, 2(2002) 369-73.
- [40] A.G. Mathad, R.M. Patrikar, The origin of surface stress experienced by a micro-cantilever beam, *Students' Technology Symposium (TechSym)*, 2010 IEEE2010, pp. 12-6.
- [41] L.J. Steinbock, M. Helm, Wavelength dependence of photoinduced microcantilever bending in the UV-VIS range, *Sensors*, 8(2008) 23-34.
- [42] S. Wu, H. Liu, T. Cheng, X. Zhou, B. Wang, Q. Zhang, et al., Highly sensitive nanomechanical assay for the stress transmission of carbon chain, *Sensors and Actuators B: Chemical*, 186(2013) 353-9.
- [43] J. Pennakalathil, J.-D. Hong, Self-standing polyelectrolyte multilayer films based on light-triggered disassembly of a sacrificial layer, *Acs Nano*, 5(2011) 9232-7.
- [44] K.H. Fries, J.D. Driskell, S. Samanta, J. Locklin, Spectroscopic analysis of metal ion binding in spiropyran containing copolymer thin films, *Analytical chemistry*, 82(2010) 3306-14.
- [45] K.H. Fries, J.D. Driskell, G.R. Sheppard, J. Locklin, Fabrication of spiropyran-containing thin film sensors used for the simultaneous identification of multiple metal ions, *Langmuir*, 27(2011) 12253-60.
- [46] Y. Huang, F. Li, C. Ye, M. Qin, W. Ran, Y. Song, A Photochromic Sensor Microchip for High-performance Multiplex Metal Ions Detection, *Scientific reports*, 5(2015).

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