**CSIRO** PUBLISHING

*Aust. J. Chem.* **2012**, *65*, 283–289
http://dx.doi.org/10.1071/CH12093

# Photoconversion of Spiropyran to Merocyanine in a Monolayer Observed Using Nanosecond Pump-Probe Brewster Angle Reflectometry

*Bernhard Siebenhofer,*[A,B,C] *Sergey Gorelik,*[D] *Anton V. Sadovoy,*[D]
*Martin J. Lear,*[E] *Hong Yan Song,*[D] *Christoph Nowak,*[A,B,F,G]
*and Jonathan Hobley*[D,G]

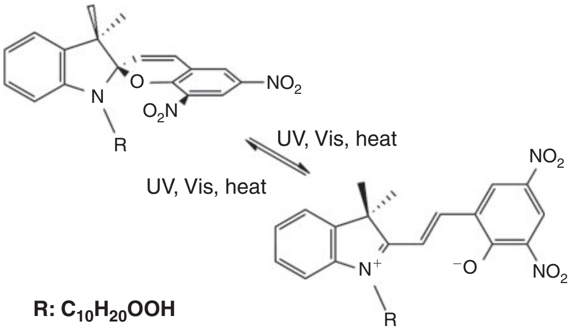
[A]Austrian Institute of Technology, AIT, Donau-City-Straße 1, 1220 Vienna.
[B]Centre for Biomimetic Sensor Science, 50 Nanyang Drive, Research Technoplaza, XFrontiers Block, Singapore 63755.
[C]University of Natural Resources and Life Sciences, Department of Nanobiotechnology, Muthgasse 11, 1190 Vienna, Austria.
[D]Institute of Materials Research and Engineering, IMRE, 3 Research Link, Singapore 117602.
[E]Department of Chemistry, National University of Singapore, 3 Science Drive, Singapore 117543.
[F]Centre of Electrochemical Surface Technology, CEST, Viktor-Kaplan-Str. 2, 2700 Wiener Neustadt, Austria.
[G]Corresponding authors. Email: hobleyj@imre.a-star.edu.sg; C.Nowak@ait.ac.at

A new apparatus for nanosecond-time-resolved Brewster angle reflectometry is described that can be used to measure transient angle-resolved reflectivity changes in thin films and monolayers in a single pulsed laser shot. In order to achieve this, a cylindrical lens is placed in the probe beam path replacing the goniometer that is usually used for angular scanning in other systems. Using two synchronized nanosecond pulsed lasers in pump-probe configuration it is possible to measure the kinetics of photoinduced conformational changes by altering the delay between pump and probe pulses. The system was used to observe nanosecond time-resolved photodynamics in a spiropyran monolayer at the air-water interface. After UV excitation the spiropyran converted to its merocyanine form in two stages. The first stage occurred with a timescale close to the instrument time resolution (tens of nanoseconds) whereas the second stage occurred over a few hundred nanoseconds.

Manuscript received: 13 February 2012.
Manuscript accepted: 20 February 2012.

## Introduction

Self assembled layers that form at interfaces between dissimilar materials are interesting regions where unique chemical reactions and biological processes can occur.[1–3] This is because within such layers the environment is quite different compared with both of the bulk media that create the interface. Molecules that exist within such regions are often highly ordered, yet fluid, states in which molecules move predominantly in two dimensions and where specific molecular interactions strongly hold the layer together.[4–7] Additionally these interfaces can exhibit potential gradients due to forced conformations of molecules at the interface.[3] However the study of reactions in such regions is somewhat limited by the fact that these ordered layers are too thin to see optically in transmission as they are sub-light wavelength in thickness and give a tiny phase shift or absorbance to light passing through them. To overcome this, several techniques have been successfully applied. On metallic surfaces surface plasmon resonance (SPR) and polarization modulation Fourier transform infrared spectroscopy (PM-FTIR) have proven to be successful at making observations.[8–11] PM-FTIR can also be used on other substrates. However, fast nanosecond kinetics of chemical processes has not been reported with either SPR or PM-FTIR. Cavity ring-down spectroscopy (CRDS) can be used to make thin film measurements by making the probe-beam travel through the sample with multiple passes, thereby increasing the effective pathlength.[12–17] However time resolution on CRDS will be limited by the multi-pass requirement. Also, small absorbance or scattering losses from the substrate are problematic with a multi-pass configuration. CRDS has therefore not yet been used for fast kinetic studies. Brewster angle microscopy (BAM) was invented as a technique to study adsorbed molecules on solids and floating monolayers at the air/liquid interface.[4–7] It is based on the fact that p-polarized light is fully refracted and therefore not reflected when it is incident at an interface at Brewster's angle. However, the presence of a monolayer on the reflecting surface alters the refractive index at the interface and some reflection occurs with an intensity that depends on the refractive index of the monolayer. This means



**Scheme 1.**

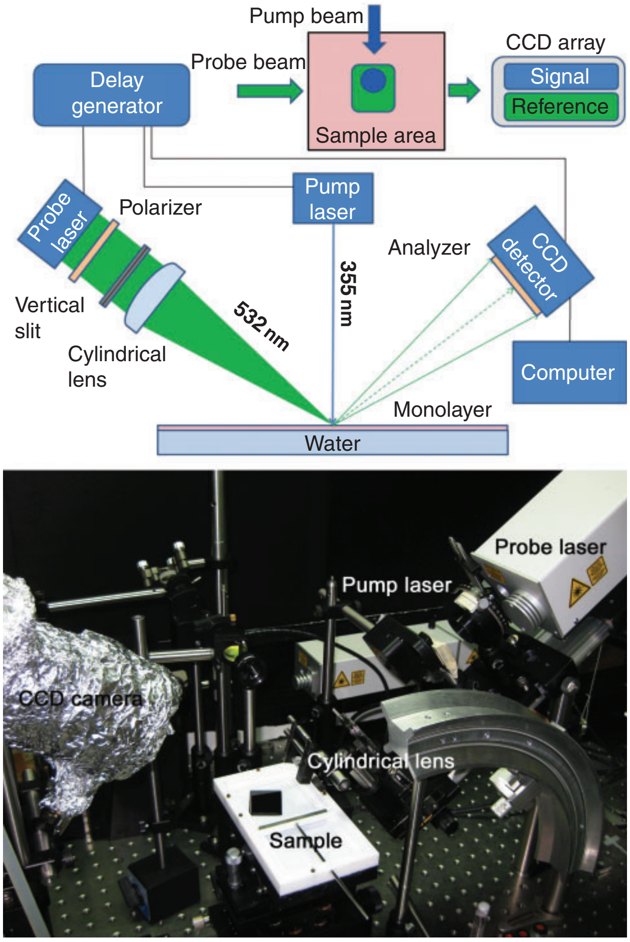


**Fig. 1.** (*Top*) Experimental setup for pump-probe Brewster angle reflectometry. The top insert shows the method of self referencing measurements. (*Bottom*) Photograph of the apparatus showing its actual layout.

that if we image a monolayer at Brewster's angle we can obtain a high contrast image of the lateral morphology of the layer with an inherently dark background. It has been shown that, using pulsed pump-probe laser configurations, it is possible to measure time-resolved events using BAM.[18–21]

Recently the present authors reported the use of Brewster angle reflectometry (BAR) to measure very small absorbance changes down to $\sim 10^{-6}$ in a single pulse transient absorption measurement in spiropyran monolayers on quartz and water. The system developed to achieve this utilized a precision motorized goniometer to scan small angle steps in the vicinity of Brewster's angle.[22,23] That work showed that transient absorption measurements in spiropyran monolayers were possible with a continuous wave (CW) probe laser and a nanosecond pulsed laser as an excitation source. In principle that apparatus could therefore achieve nanosecond time-resolution, however this was not demonstrated in that work. One drawback of the technique was that the angle resolution was only achievable with a precise goniometer and by scanning the angle whilst measuring many kinetic traces. This method is effective for single shot kinetic traces, but a more cost-effective approach may be attractive. Also it may sometimes be desirable to determine the angle dependence in a single shot.

This work describes the development of an alternative strategy for BAR, using a fixed angle for the incident laser whilst still achieving angle resolution, by using a cylindrical lens to achieve a range of angles at the sample on the interface. This eliminates the need for an expensive precision motorized goniometer. The new apparatus was used to make observations on photoactive spiropyran monolayers at an air-water interface.

Amphiphilic spiropyrans (Scheme 1) can often form monolayers at an air-water interface.[19–22,24–26] When colourless spiropyran is irradiated by UV light it converts to a ring-open planar merocyanine with increased dipole moment and which also absorbs visible light.[27–32] In the dark or photochemically, merocyanine converts back to spiropyran. Although many works describe the photoactivity of spiropyran monolayers, very few actually attempt to mechanistically understand the photoconversion of the spiropyran to its merocyanine.[24–26] This lack of mechanistic study is no doubt because transient measurements have been hampered by the short optical path-length of the monolayer. The current work aims to give information on the kinetic processes in a spiropyran monolayer on water following pulsed UV excitation and to determine the rate of formation of the merocyanine form of the molecule.

## Experimental

### *Brewster Angle Microscope*

Two types of BAR apparatus are used in this work. The first has been described previously[22,23] and is essentially based on a NanoFilm EP3$^{\mathrm{TM}}$ BAM with nanosecond laser excitation, except that it has an additional photomultiplier tube (PMT) detector, connected to a Tektronics Oscilloscope (TDS 2014B 1GS $s^{-1}$, 100 MHz) with $50\,\Omega$ termination for determining nanosecond kinetics of reflectivity change. This apparatus was used both to visualize the monolayer (with its CCD camera) and to determine kinetic information (with its PMT) after UV excitation of the monolayer. The new BAR apparatus developed in this work was custom built (Fig. 1): A pulsed probe laser (8 ns, 532 nm, 10 Hz Nd : YAG Litron Laser Nano-L-280–10, 140 mJ) was mounted on a sloped platform approximately set to the calculated Brewster-angle of the air-water interface. The probe light was p-polarized using a Glan-Taylor polarizer. A combination of a vertical slit and a cylindrical lens were used to focus a vertical slit cross-section of the initially round laser beam onto a point on the sample surface so that the incident beam has varying angles of incidence at the sample as determined by the focal length of the cylindrical lens. The reflected beam therefore diverges over a range of angles. As the approximate centre of the laser beam is incident at the Brewster angle, reflectivity will be minimized there. According to Fresnel's equations for p-polarized light this leads to a parabolic reflectivity increase around Brewster's angle.[23]

The reflected light was collected using a charge-coupled device (CCD) camera (DU420-BV, Andor Technology).

The probe laser was appropriately attenuated using neutral density filters so it did not saturate the camera. This camera features a two dimensional array of pixels that allows the collection of the fully expanded probe beam on a shot to shot basis. For dark current reduction the camera is thermoelectrically cooled to −80°C. Additionally the CCD chip was analyzed in two halves. One-half measured the intensity profile of probe light that had reflected from a UV irradiated region on the sample and the other half monitored light from a non-irradiated part of the sample. The irradiated and non-irradiated zones were controlled by inserting a razor blade to partially mask the sample on the probed area. In this way every pulsed laser shot had its own internal reference (no-pump) beam so that reflectance changes and angular shifts could be accurately determined without shot to shot noise due to beam profile changes or noise from vibrations in the laboratory. In this case the main noise is expected to be shot-to-shot noise in the pump-laser beam intensity (usually ~10 %).

The 8 ns pulse from a Litron NANO-S-60–30 Nd : YAG laser was used to excite the sample. Either 355 nm 3rd or 266 nm 4th harmonics can be used depending on the respective samples absorption spectrum. The laser was equipped with a variable attenuator that could be used to vary the output energy from 0–10 mJ for 355 nm and 0–6 mJ for 266 nm. A Plano-convex lens was used to reduce the pump laser spot size to a diameter of ~2 mm on the sample surface. Maximum fluences of ~120 mJ cm$^{-2}$ were estimated for this configuration.

Two delay generators (Stanford Research Systems DG535 and Berkley Nucleonics Corporation BNC-465) were used to synchronize the flashlamps and Q-switches of each laser, both lasers relative to each other and to the shutter of the CCD camera. Variation of the delay time between the pump and probe lasers allowed the measurement of kinetics with nanosecond time resolution. The time-resolution is limited only by the temporal convolution of pulse lengths of the pump and probe lasers.

For measurements on spiropyran monolayers a high intensity white light source (Thorlabs OSL1-IC Fibre Illuminator, 150 W) was used to fully photobleach the monolayer back to the spiropyran form before the experiments on photocoloration kinetics were started. This was done because the equilibrated form of this particular spiropyran is predominantly the merocyanine form if the sample is left in the dark.[27–31]

### Sample Preparation

A small Langmuir-Blodgett trough (7.5 cm by 0–12 cm surface area) was cleaned using ethanol, acetone, chloroform, and deionized water. The bulk liquid sub-phase was deionized water (ELAGA Laboratory Water, Purelab option-Q). The floating layer was deposited using a Hamilton micro-syringe. The photochromic dye solution was added drop by drop with the needle parallel and as close as possible to the surface without actually touching it. Before use the syringe was cleaned with ethanol, acetone, chloroform, and deionized water. The monolayer was compressed to give a molecular monolayer with 0.34 nm$^2$ molecule$^{-1}$.

Amphiphilic spiropyran, 11-(3′,3′-dimethyl-6,8-dinitrospiro[chromene-2,2′-indoline]-1′-yl) undecanoic acid, was synthesized from 2,3,4-trimethylindolenium 11-bromoundecanoic acid and 3,5-dinitrosalicylaldehyde via a two-step substitution and condensation reaction.[22,23]

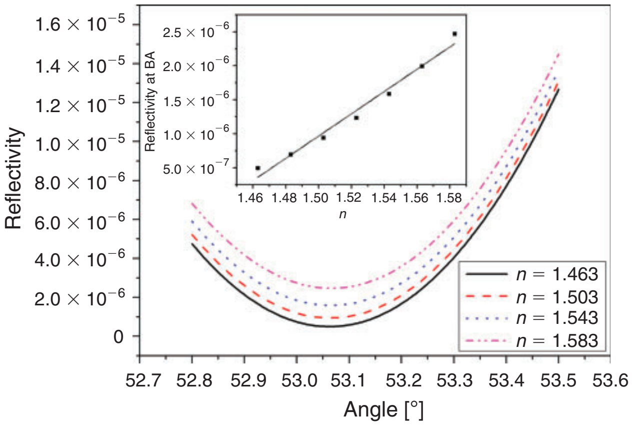


**Fig. 2.** Simulation of Brewster angle minimum upon variation of the real part of the refractive index.

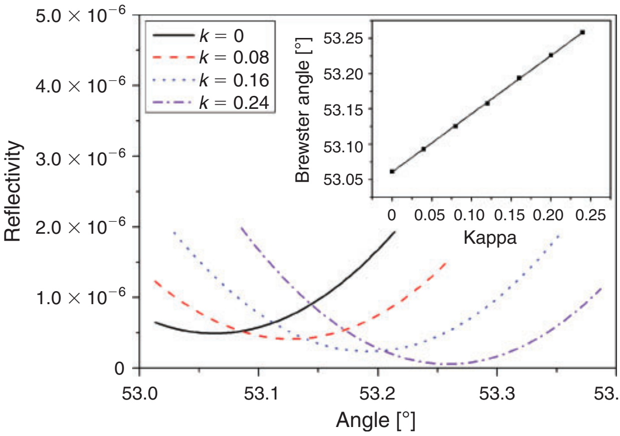


**Fig. 3.** Simulation of Brewster angle minimum upon variation of the imaginary part of the refractive index.

## Results and Discussion

### Theoretical Considerations

The reflectivity and transient absorption changes of the interface can be simulated using Fresnel equations.[21–23] For this work WINSPALL (Jürgen Worm, MPIP Mainz) is used. This software can be used to compute the reflectivity of multilayer systems utilizing Fresnel equations and matrix formalism. Figs 2 and 3 show the behaviour of Brewster's angle upon variation of real and imaginary part of the refractive index of a floating monolayer on water. This shows that a one shot Brewster angle measurement can be used to simultaneously access transient absorption via the imaginary part of refractive index Kappa ($\kappa$) and reflectivity changes caused by changes in $n$, the real part of refractive index. Additionally it can be seen that the angular shift with absorption is linear over the range of values simulated, which are also the range of angular shifts found experimentally. In addition, the change in the reflectivity with the real part of refractive index can be approximated to linear (with slight deviation) over the range of intensity changes found in this work.

### Spiropyran Monolayer Characterization and Kinetics

Fig. 4 shows a BAM image of a monolayer made by 30 μL of a 1 mM spiropyran in chloroform spreading solution on an area of

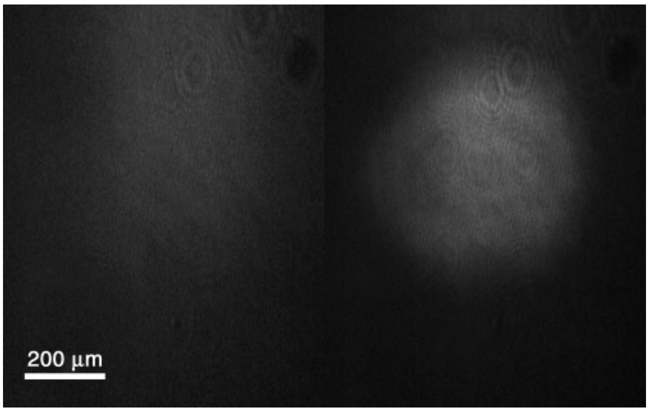


**Fig. 4.** BAM image of a spiropyran monolayer recorded with modified Nanofilm EP3$^{TM}$. The right part of the image shows the reflectivity change after one shot irradiation at 355 nm.

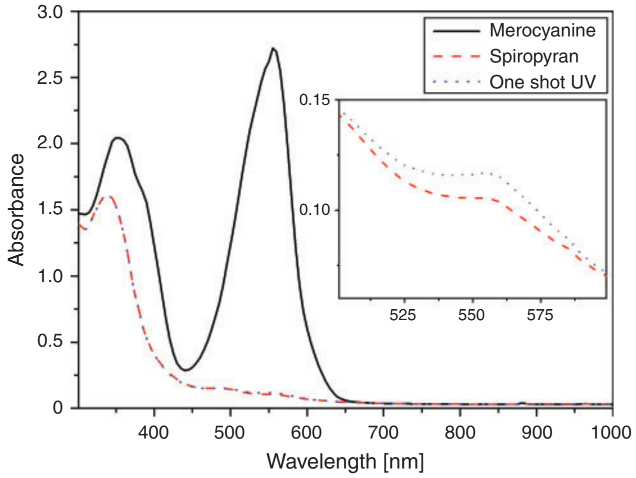


**Fig. 5.** Spiropyran and merocyanine absorption spectrum in chloroform. Insert shows the increase in absorbance after a single, 355 nm pulse of laser excitation at the same fluences used in the kinetic studies. In this case the measurement is in a 0.5 cm quartz cell.

67.5 cm$^2$ ($\sim$0.34 nm$^2$ molecule$^{-1}$). From this picture it is evident that the layer is homogeneous enough for obtaining reliable self referenced measurements. In this image it can be seen that the reflectivity of the monolayer increases in the region irradiated by the UV laser. The reflectivity change was reversible and the irradiation did not lead to destruction of the monolayer or the molecules within the monolayer. All further studies are done on monolayers with exactly this surface coverage.

Fig. 5 shows the absorption spectra for the spiropyran and merocyanine form of the molecules used in the monolayers in chloroform. The peak maximum is at $\sim$560 nm, however because water is more polar than chloroform we may expect a significant blue shift of tens of nm in the monolayer.[31] Also in Fig. 5 we can see the absorption change in a 0.5 cm pathlength small volume cell upon a single pulse of 355 nm 10 mJ excitation of spiropyran. The entire cell volume was irradiated and the laser pulse was nearly 90 % absorbed. We can see that despite the high absorbance of the 355 nm pulse by the spiropyran the absorbance increase is only $\sim$0.01. This means that the conversion to the merocyanine in the monolayer is expected to be very small, since the monolayer absorbance would only be $\sim 10^{-3}$ at 355 nm.

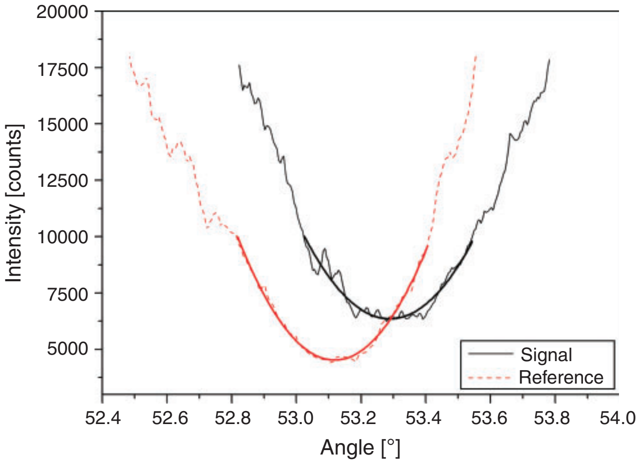


**Fig. 6.** Reflectivity changes in the irradiated part of the sample (signal) compared with the reflectivity of the non-irradiated part (reference) measured directly from the two halves of the Andor CCD camera (4 μs pump-probe delay). Parabolic fits are shown for each curve.

Fig. 6 shows typical single shot signal for reflectivity changes for a 355 nm excited monolayer compared with its reference reflectivity angular dependence. The minima of the datasets can be adequately fitted by a parabolic function and this fitting protocol is used to determine both the intensity and angular shifts for the kinetic studies.

Figs 7 and 8 show the kinetics of angular and intensity shift for the spiropyran monolayer. The rise in reflectivity corresponds to a rising value of the real part of the refractive index. The Brewster-angle shift to greater angles means that the transient absorption of merocyanine is bigger than that of spiropyran, as expected. These results are in good agreement with previous works by Gorelik et al.[22]

The kinetics determined from the single shot angle dependent measurements with different time delays are consistent with a two-step mechanism for the ring opening of the spiropyran. According to this data, the first stage has a lifetime of $\sim$30 ns and is therefore highly convoluted into the time response for the system which is determined by the temporal overlap of the pump and probe pulses. The second stage in the reaction is much slower and has a lifetime of 230 ns (angular shift) and 570 ns (intensity shift). We can therefore estimate the lifetime to be on the order of a few 100 ns, as this difference is not significant compared with the experimental noise.

Fig. 9 shows the angular shift dependency on the pump laser power. The dependence is approximately linear and the maximum conversion achieved at the highest fluence was 10 % spiropyran to merocyanine. This is consistent with the low conversions achievable in chloroform solution. In fact this particular spiropyran appears to have a very low quantum yield for coloration compared with its high quantum yield for bleaching.[22,27–32]

It is worth commenting on the fluences that the monolayer is exposed to without apparent damage, or saturation effects. First, exact laser fluences are rather hard to determine as the exact spot size is rather uncertain, so the values given should be considered somewhat relative. Second, saturation is not apparent and the photochemistry appears to be single photon in nature. We attribute this to the inherently low quantum yield for photo-merocyanine formation for this compound. We should also consider temperature effects and possible destruction of the monolayer. In fact the monolayer will absorb $\sim$1/1000th of the

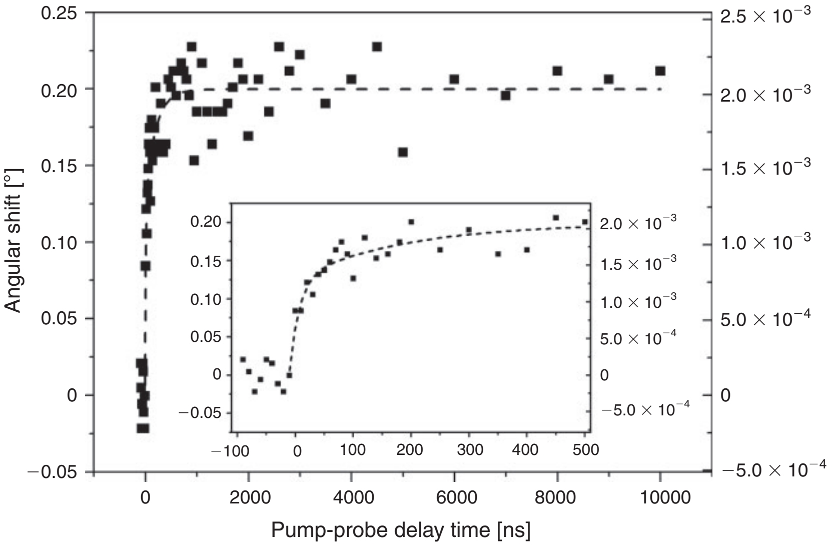


**Fig. 7.** Kinetics of the angular shift in a pumped spiropyran monolayer and its exponential approximation. Axis legends of the insert are identical to the main graph.

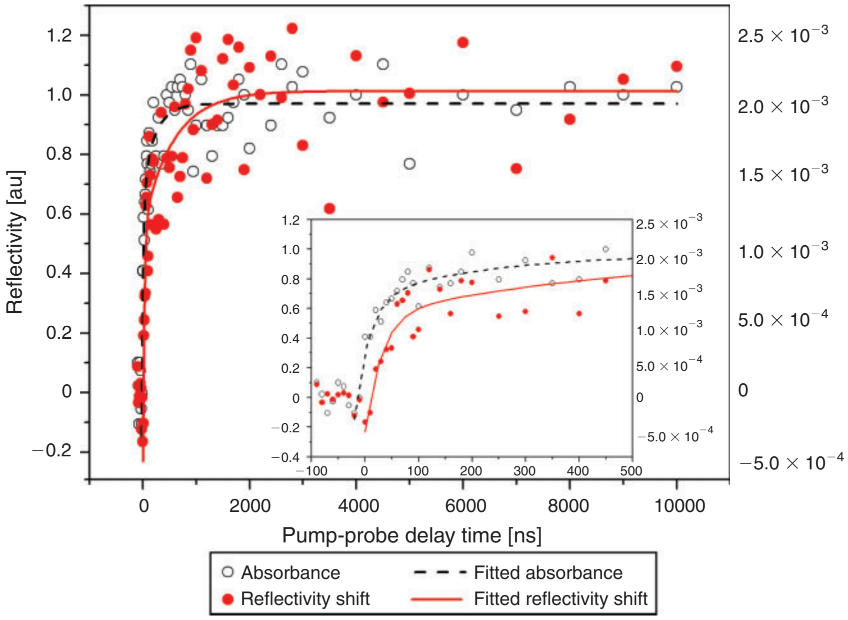


**Fig. 8.** Kinetics of the intensity shift in a pumped spiropyran monolayer and its exponential approximation with angular shifts for comparison. Axis legends of the insert are identical to the main graph.

incident laser beam (i.e. a maximum of ~0.3 mJ cm$^{-2}$). This energy would be expected to dissipate to the sub-phase, which has a high heat capacity, on the picosecond timescale,[20] hence the monolayer is unlikely to get hot enough to damage. This is verified in BAM images which show reversible reflectivity changes without monolayer damage, as exemplified in Fig. 4.

For comparison, the current methodology was compared with the EP3 system at a single angle of reflection using the photomultiplier detector. This data is shown in Fig. 10 with the fits from the reflectivity and angular shifts determined with the newer apparatus. It is quite apparent that both systems give very consistent kinetic traces, giving us confidence in the kinetics that can be derived.

Therefore with some confidence we can state that the transformation from spiropyran to merocyanine in the monolayer occurs in two stages. The first occurs in several tens of nanoseconds and the second occurs in several hundred nanoseconds. Two scenarios could account for these observations, and these will be explored next.

The first possibility is that the mechanism involves a fast singlet manifold and a slower triplet manifold. Non-nitrated spiropyrans are known to convert to their merocyanines very rapidly in sub-nanosecond timescales[28] and the fast component in the current case could then be singlet state conversion to merocyanine on similar timescales. Should a triplet state of spiropyran form it would be quenched by oxygen in the subphase in ~200 ns, since the solubility of oxygen in water is ~$10^{-3}$ M and with an expected quenching rate constant of ~$5 \times 10^{9}$ dm$^{3}$ mol$^{-1}$ s$^{-1}$.[33] This timescale is consistent with the current experimental observation and a triplet manifold may

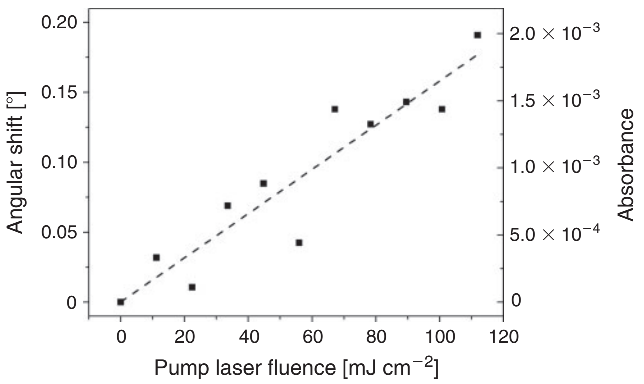


**Fig. 9.** Angular shift at 1 μs pump probe delay time depending on pump laser fluence.

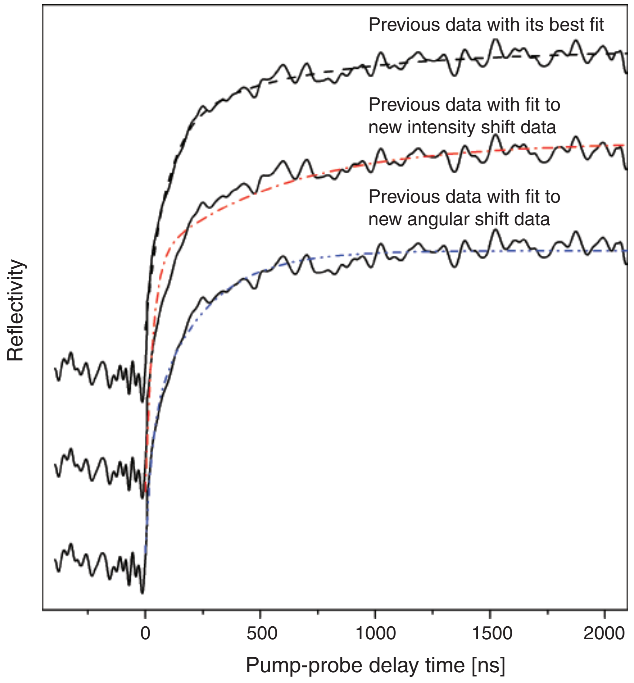


**Fig. 10.** Comparison of the fits obtained to data from the new methodology, with the data and fit for the previously reported method with angle scanning (data averaged for 5 transient measurements). The comparison data (fit from data) fits to lifetimes of ~90 ns and ~600 ns.

therefore be appealing as an assignment for the longer component, with its lifetime controlled by oxygen quenching. However, diffusion constants in air are ~$10^5$ times greater than in water,[34] so triplet state quenching should be very rapid at the air-water interface, too rapid to account for the longer timescale process in the photoconversion in the monolayer. A second explanation for the observations must therefore be sought.

Obviously some rapid events occur on a timescale similar to the pulse duration, and these can be excited singlet state formation and possibly formation of a merocyanine isomer *cis* about the central double bond. We can suggest that, since the monolayer is quite densely packed, it may be that the formation of the merocyanine isomers that are *trans* about the central double bond may be retarded compared with the reaction in solution. Additionally molecules in a monolayer are likely to be far more constrained in terms of their geometry compared with molecules in solution. This would also be expected to slow down the process of isomerization from *cis*- to *trans*-forms.

## Conclusions

An apparatus was constructed that allows easy one-shot angle-resolved reflectivity measurements, probing Brewster's angle and its vicinity simultaneously. Qualitative measurements on organic photochromic dyes have shown that the setup is feasible for conversion kinetics measurements on monolayers on water. Spiropyran films studied in this way exhibited rather slow photoconversion to the final merocyanine over a few hundred nanoseconds, probably because of steric hindrance to bond rotations in the packed monolayer.

## Acknowledgements

This work was funded by the International Graduate School Bio-Nano-Tech, a joint venture of University of Natural Resources and Life Sciences Vienna (BOKU), the Austrian Institute of Technology (AIT) and the Nanyang Technological University (NTU). Equipment and materials were supported by A-STAR JCO and A-STAR-JST funding.

## References

[1] P. Schaaf, P. Dejardin, A. Schmitt, *Langmuir* **1987**, *3*, 1131. doi:10.1021/LA00078A045
[2] A. Ulman, *Chem. Rev.* **1996**, *96*, 1533. doi:10.1021/CR9502357
[3] S. Kajimoto, N. Yoshii, J. Hobley, H. Fukumura, S. Okazaki, *Chem. Phys. Lett.* **2007**, *448*, 70. doi:10.1016/J.CPLETT.2007.09.077
[4] S. Henon, J. Meunier, *Rev. Sci. Instrum.* **1991**, *62*, 936. doi:10.1063/1.1142032
[5] D. Hoenig, D. Möbius, *J. Phys. Chem.* **1991**, *95*, 4590. doi:10.1021/J100165A003
[6] D. Hönig, D. Möbius, *Thin Solid Films* **1992**, *210–211*, 64. doi:10.1016/0040-6090(92)90169-C
[7] S. Siegel, D. Hoenig, D. Vollhardt, D. Moebius, *J. Phys. Chem.* **1992**, *96*, 8157. doi:10.1021/J100199A062
[8] K. Sasaki, T. Nagamura, *Appl. Phys. Lett.* **1997**, *71*, 434. doi:10.1063/1.119571
[9] R. B. M. Schasfoort, A. J. Tudos, *Handbook of Surface Plasmon Resonance* **2008** (RSC Publishing: Cambridge, UK).
[10] B. L. Frey, R. M. Corn, S. C. Weibel, Polarization-Modulation Approaches to Reflection Absorption Spectroscopy, in *Handbook of Vibrational Spectroscopy* **2001**, Volume 2, pp. 1042–1056 (Eds J. Chalmers, P. R. Griffiths) (John Wiley & Sons: Chichester, UK).
[11] S.-H. Kim, H.-J. Suh, K.-N. Koh, S.-A. Suck, H.-J. Choi, H.-S. Kim, *Dyes Pigments* **2004**, *62*, 93. doi:10.1016/J.DYEPIG.2003.08.006
[12] D. Kleine, J. Lauterbach, K. Kleinermans, P. Hering, *Appl. Phys. B* **2001**, *72*, 249.
[13] J. A. Piest, M. Anni, R. Cingolani, G. Gigli, *Synth. Met.* **2008**, *158*, 1062. doi:10.1016/J.SYNTHMET.2008.02.015
[14] I. M. P. Aarts, B. Hoex, A. H. M. Smets, R. Engeln, W. M. M. Kessels, M. C. M. van de Sanden, *Appl. Phys. Lett.* **2004**, *84*, 3079. doi:10.1063/1.1713047
[15] R. N. Muir, A. J. Alexander, *Phys. Chem. Chem. Phys.* **2003**, *5*, 1279. doi:10.1039/B212790C
[16] C. Zhu, B. Xiang, L. Zhu, R. Cole, *Chem. Phys. Lett.* **2008**, *458*, 373. doi:10.1016/J.CPLETT.2008.04.125
[17] X. Wang, M. Hinz, M. Vogelsang, T. Welsch, D. Kaufmann, H. Jones, *Chem. Phys. Lett.* **2008**, *467*, 9. doi:10.1016/J.CPLETT.2008.10.086
[18] J. Hobley, T. Oori, S. Kajimoto, K. Hatanaka, G. Kopitkovas, T. Lippert, H. Fukumura, *Colloid Surface A* **2006**, *284–285*, 514. doi:10.1016/J.COLSURFA.2005.12.002
[19] J. Hobley, T. Oori, S. Kajimoto, S. Gorelik, D. Hönig, K. Hatanaka, H. Fukumura, *Appl. Phys. A–Mater.* **2008**, *93*, 947. doi:10.1007/S00339-008-4742-5
[20] J. Hobley, S. Gorelik, T. Oori, S. Kajimoto, H. Fukumura, J. Matsui, T. Miyashita, *Biointerphases* **2010**, *5*, FA105. doi:10.1116/1.3507241

[21] J. Hobley, T. Oori, S. Gorelik, S. Kajimoto, H. Fukumura, D. Hönig, *J. Nanosci. Nanotechnol.* **2009**, *9*, 1. doi:10.1166/JNN.2008.N03

[22] S. Gorelik, J. Hobley, M. J. Lear, H-Y. Song, S. Y. S. Yong, J. Cheng, *Int. J. Nanosci.* **2009**, *8*, 213.

[23] S. Gorelik, H.-Y. Song, M. J. Lear, J. Hobley, *Photochem. Photobiol. Sci.* **2010**, *9*, 141. doi:10.1039/B9PP00105K

[24] M. Matsumoto, T. Nakazawa, R. Azumi, H. Tachibana, Y. Yamanaka, H. Sakai, M. Abe, *J. Phys. Chem. B* **2002**, *106*, 11487. doi:10.1021/JP0214716

[25] T. Minami, N. Tamai, T. Yamazaki, I. Yamazaki, *J. Phys. Chem.* **1991**, *95*, 3988. doi:10.1021/J100163A020

[26] E. E. Polymeropoulos, D. Möbius, *Ber. Bunsenges. Phys. Chem* **1979**, *83*, 1215.

[27] M. Bletz, U. Pfeifer-Fukumura, U. Kolb, W. Baumann, *J. Phys. Chem. A* **2002**, *106*, 2232. doi:10.1021/JP012562Q

[28] J. Hobley, M. J. Lear, H. Fukumura, in *Photochemistry of Organic Molecules in Isotropic and Anisotropic Media* **2003** (Eds V. Ramamurthy, K. S. Schanze) (Marcel Dekker: New York, NY).

[29] J. Hobley, V. Malatesta, *Phys. Chem. Chem. Phys.* **2000**, *2*, 57. doi:10.1039/A908360J

[30] J. Hobley, V. Malatesta, W. Giroldini, W. Stringo, *Phys. Chem. Chem. Phys.* **2000**, *2*, 53. doi:10.1039/A908356A

[31] J. Hobley, V. Malatesta, R. Millini, L. Montanari, W. O. N. Parker, *Phys. Chem. Chem. Phys.* **1999**, *1*, 3259. doi:10.1039/A902379H

[32] D. A. Reeves, F. Wilkinson, *J. Chem. Soc., Faraday Trans.* **1973**, *2*, 1381.

[33] J. Hobley, F. Wilkinson, *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1323. doi:10.1039/FT9969201323

[34] D. R. Lide, H. P. R. Frederiske (Eds), *CRC Handbook of Chemistry and Physics* **1996**, 77th Edition, Section 6, pp. 218–221 (CRC Press: New York, NY).