

# Surface Degradation of Spiropyran based films

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## Abstract

Coatings with photoswitchable polarity can allow for control over the physical properties of surfaces. Such coatings can be prepared by combining molecular photoswitches with other molecular components that formation of amorphous films rather than crystallisation. Here, a thioctic acid unit was combined with a spiropyran photochromic switch to form spiropyran thioctic ester (**SPTE**), which can form amorphous films, melting at a relatively low temperature (70-90 °C). The photochromism of the films is reversible however, we show that the increase in surface polarity observed upon switching with UV light to the merocyanine isomer is due in part to degradation not observed in the bulk of the film. Vibrational spectroscopy show the initial switching to the merocyanine state occurs but the prolonged exposure leads to degradation of the merocyanine formed. The dithiolane unit of the **SPTE** is shown to be innocent in regard to degradation by comparison with a non-substituted nitrospiropyran (**NSP**). The films, subjected to extended irradiation, were monitored by DR- and ATR-FTIR, UV/vis absorption and Raman spectroscopy. The suitability of each of the techniques to report on the state of the surface of the film, of relevance to contact angle measurements, is determined and insight is gained into both the stability of the spiropyran photoswitch in and near the surface of the coating, as well as the pathways to degradation.

## Introduction

Smart coatings, coatings that change their properties upon application of an external stimulus, are of interest in controlling surface interactions, and have potential in engineering existing materials to create new and improved properties.<sup>1</sup> Molecular based materials for photoresponsive surfaces, for example with controllable wettability, provide particular opportunities,<sup>2</sup> as organic photoswitches are chemically tunable in structure, dipole moment, and wavelength of photoactivation.<sup>3,4</sup> Several classes of molecular photoswitches are widely applied in creating responsive materials with controllable wettability, include azobenzenes,<sup>5</sup> spiropyrans,<sup>6</sup> and diarylethenes.<sup>7</sup>

Surface energy is typically determined through surface wettability, primarily through solvent contact angle measurements, and hence the response of a modified surface to light can be assessed readily by monitoring the shape of a drop of solvent on the surface of interest. However, changing the wettability of a coated surface, for example, by changing the polarity of the material at the surface, is insufficient to achieve a large change in contact angle.<sup>8</sup> Indeed surface structure is the primary determinant in regard to the wettability of a material, as demonstrated elegantly in the work of Uchida and coworkers using diarylethene based compounds that change wettability under irradiation with UV light.<sup>9-11</sup> The isomers of this photochromic switch have different melting points and when a coating of microcrystals of the open isomer is irradiated, a eutectic mixture forms and melts, and then recrystallizes to form a different crystal morphology (smaller crystals) on the surface as the mole fraction of the closed form increases. In this way the roughness of the surface can be switched with large changes in contact angle induced due to the difference in topology.<sup>12-17</sup> This work demonstrates elegantly that a large change in surface wettability can be generated using a change in the microstructure of a surface even if the polarity of the coating itself does not

change.

In contrast to diaryl ethene photoswitches, the photochromic spiropyrans show a large change in dipole moment, increasing on changing from the spiropyran to the merocyanine isomer (15 Debye).<sup>18–20</sup> Spiropyrans have been studied extensively in solution for their switching properties, as well as their response to stimuli such as acid, base, heat, *etc.*<sup>21</sup> The nitro substituted spiropyran **NSP**, in particular, is well studied for its photochromic properties and its ability to switch between two isomers upon irradiation with UV-light (figure 1).

In tuning responsive behaviour at the boundaries of material interfaces, not only the specific desired property needs to be considered. Other processes that impact on the reversibility and fatigue resistance of the smart coating are important, since for most applications reversible switching without fatigue over multiple cycles is required.

Reactions due to external stimuli that cause degradation are well studied in solution. However, degradation upon switching is less frequently studied in polymer and amorphous materials.<sup>3</sup> Furthermore, it is not necessarily the case that the same degradation pathways observed in solution are followed also in solid or amorphous materials, and fatigue needs to be understood also in the solid state if they are to be incorporated in material applications.<sup>3</sup> In the case of spiropyrans, switching and the fatigue over switching cycles is studied extensively in solution with aggregation of the switch in the merocyanine state cited as a major cause of fatigue.<sup>22,23</sup>

When designing a functional coating, interference between the support (*e.g.*, a polymer backbone) and the switch used to generate a change in wettability should not occur.<sup>3,24</sup> The material also needs to be crafted into a structured coating to maximise changes in solvent contact angle. A candidate for such structured switchable films are those based on the thiocetic acid (**TA**) motif, which contains a five membered disulfide ring connected with an alkyl carboxylic acid chain (figure 2).<sup>25</sup> The disulfide is oxidized at metallic surfaces and forms self assembled monolayer by chemisorption onto gold or other noble metals. However, this disulfide moiety is also applied in dynamic polymerization with reversible or self healing

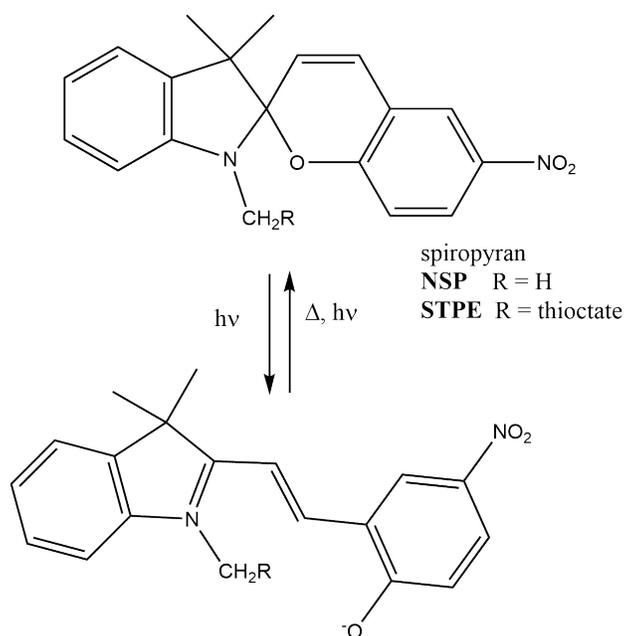


Figure 1: Interconversion between the Spiropyran and merocyanine isomers of **NSP** and **STPE**

polymers formed upon heating of thiocetic acid (figure 2).<sup>26–29</sup>

In 1954, Reed et al., while studying the synthesis of DL- $\alpha$ -lipoic Acid (Thiocetic acid) noted

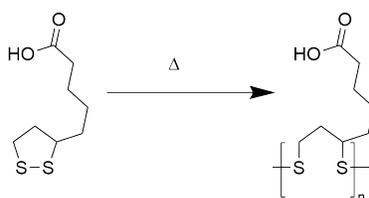


Figure 2: Thermal polymerisation of thiocetic acid

sticky polymers produced as by-products in the final oxidation step. These by-products turned out to be linear polymers formed through the breaking and forming of disulfide bonds.<sup>30</sup> The polymers were synthesized intentionally using lipoic acid by heating it at 65°C for 15 min.<sup>31</sup> Co-polymers synthesized from lipoic acid and 1,2-dithiane demonstrated the formation of polycantane (ring) structures,<sup>32</sup> characterized by <sup>1</sup>H-NMR spectroscopy.<sup>33</sup> Self healing polymers can be prepared by crosslinking with 1,3 diisopropylbenzene (DIB) using FeCl<sub>3</sub>.<sup>27</sup> The dynamic nature of the thiocetic acid polymer could be suitable for surface structure adaptation and incorporation of molecular switches makes it interesting to study further

towards this application. An extensive study on the polymerization of TA and derivatives was reported by Kisanuki et al.<sup>34</sup> where they noted that polymerisation is obtained only upon melting, as the thiol compounds act as chain transfer agents and a low load of thiol compounds already limits the number average molecular weight (**Mn**). Photo decomposition of the polymers by UV irradiation was believed to changed the interlocked rings to non interlocked rings reducing the **Mn** of the polymer.

Disulfide polymerization can be initiated either with radical or anionic initiators. Most studies focus on anionic polymerization where an anionic initiator is used.<sup>35</sup> Matile and co-workers reported the synthesis of disulfide polymers in solution, via ring opening disulfide exchange polymerization (RODEP).<sup>36-38</sup> Other studies, however, show radical polymerisation in disulfide based polymers.<sup>39</sup> A combination of a self-healing polymerizable material and a switch attached to the monomer could provide a versatile material being able to both switch properties and be crafted into a structure with the added ability to self-heal.

In this contribution, we focus on the switching behaviour of nitrospiropyran (**NSP**) and its thioctic ester modified analogue (**SPTE**), used earlier to form self-assembled monolayers on gold surfaces by Ivashenko et al.,<sup>25</sup> As discussed above surface structure maximises change in surface energy achieved and the dithiolane unit is in the first instance expected to polymers at temperatures suitable for introducing surface structure by thermal embossing.<sup>39</sup> in the present, study we show that thermally induced polymerisation does not occur, but **STPE** still forms amorphous films. We focus on the photochemical stability of the **NSP** motif at the surface of these films, as it is used regularly to control the surface energy of coatings, and show differences in stability between the bulk and surface of **SPTE** films The techniques used to study the surface of thin films of **SPTE** and **NSP** determine which components in the material are observed. The wettability is determined by the layer of molecules at the surface of the film and hence the focus is placed on understand stability at the surface of the films using vibrational spectroscopies, providing insight into photoswitching of spiropyrans

in the solid amorphous states and especially the degradation pathways involved.

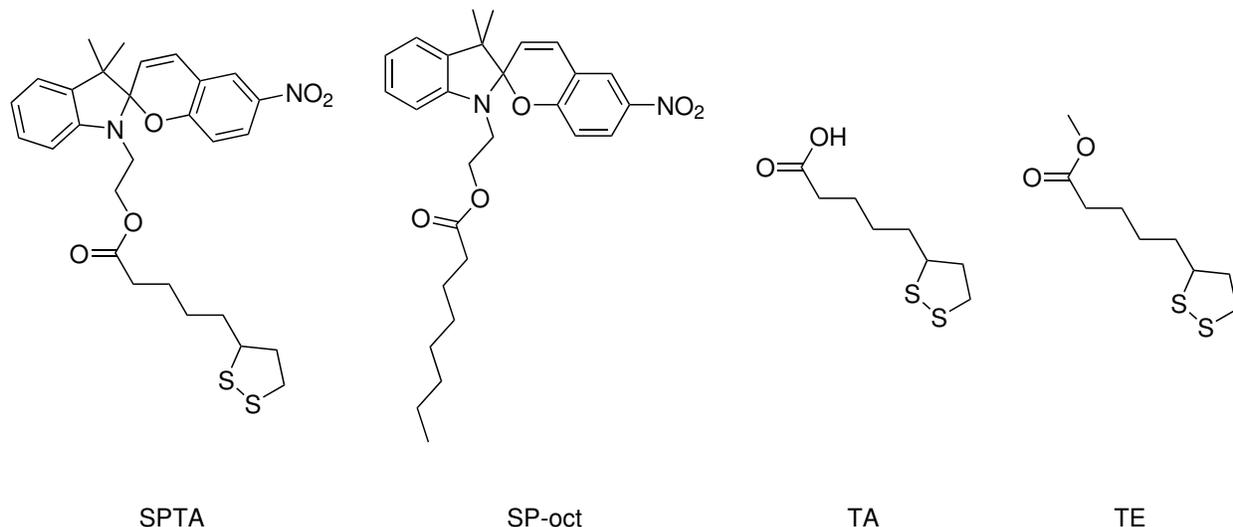


Figure 3: **SPTE** and the model compounds, a octanoic ester substituted spiropyran **SP-oct**, thioctic acid **TA** and the methyl ester of thioctic acid **TE**.

## Results and discussion

Spiropyran thioctic ester (**SPTE**) was synthesized using a Steglich esterification of the ethanol substituted nitro-spiropyran, prepared by condensation of an indoline and a para-nitrosalicylaldehyde as described earlier, with thioctic acid (Figure S1).<sup>25,40</sup> The FTIR absorption spectrum of **SPTE** shows minor differences compared to the parent compound **NSP**, specifically additional bands due to the thioctic ester moiety. The typical absorption bands of the ring closed form, such as the symmetric nitro stretch at  $1337\text{ cm}^{-1}$ , the asymmetric C-O-C mode at  $1273\text{ cm}^{-1}$ , the N-C<sub>spiro</sub>-O band at  $956\text{ cm}^{-1}$  and the out of plane ring deformation modes at  $747$  and  $809\text{ cm}^{-1}$  are observed. The UV/Vis absorption spectra of **NSP** and **SPTE**, are identical in the spiropyran (SP) and merocyanine (MC) states, indicating negligible perturbation of the electronic structures by the thioctic acid ester moiety in **SPTE**. Photoswitching from the SP to the MC isomers proceeds rapidly for both **NSP** and **SPTE**, followed by slower thermal recovery. The rate of recovery is sensitive to solvent con-

ditions and especially acidity indicating that some protonation assisted switching occurs.<sup>41</sup> Only minor degradation was observed over multiple switching cycles, however, exposure to continuous irradiation at 365 nm resulted in degradation over time, which was slowed but not halted by exclusion of O<sub>2</sub>.

## Thermal behaviour of SPTE and impact of impurities

The TA unit of **SPTE** was incorporated with the intention to allow for formation of amorphous films of the nitrospiropyran when drop cast, or spin coated, on surfaces. However, heating of solid **SPTE** to form a melt to initiate polymerisation was unsuccessful. Indeed, the batch of **SPTE** used, which contained <1 % impurities (by <sup>1</sup>H NMR spectroscopy), did not show physical processes (by Differential Scanning Calorimetry) between 0 to 85 °C (figure S2a), indicating that thermal polymerization of the dithiolane units does not occur. Thermogravimetric analysis (**TGA**) showed that the **SPTE** monomer was stable up to 168 °C under nitrogen whereafter degradation (mass loss) occurs (figure S2b). As mention in the introduction polymerization of thioctic acid requires it to melt first,<sup>34</sup> and hence the as-prepared **SPTE** is not expected to undergo thermally induced polymerisation nor melt at a low enough temperature for embossing surface structure.

However, the melting point of **SPTE** showed batch to batch variation in thermal properties presumed to be due to residual solvent and other impurities. Indeed a second batch of **SPTE**, which showed melting at 70°, contained, by <sup>1</sup>H-NMR spectroscopy, residual of 4-dimethylaminopyridine (**DMAP**) used during synthesis (figures S3, S4). The suppression of melting point by impurities could allow for lower temperature embossing of films (to introduce surface structure) and allow for polymerisation of the dithiolane unit.

Several impurities; ethanol, toluene and DMAP (< 1% ) were added to the batch showing the highest melting temperature to test the effect of each potential contaminant and therefore also on the ability for **SPTE** to undergo thermal polymerization. Melting and spreading out of the compound upon heating on a glass slide was observed for all samples, but only the

sample with DMAP remained as an amorphous material while as-prepared **SPTE**, and solvent doped **SPTE** formed microcrystals upon cooling. The presence of DMAP, in addition to suppressing the melting point, allows for formation of amorphous homogenous films and in addition to radical polymerisation triggered thermally, could trigger anionic polymerization, due to its nucleophilicity and basicity.

A sample of the batch of **SPTE** containing DMAP was heated in a closed vial to between 80 to 110 °C, after which it was allowed to cool before dissolution in THF. The THF solution was used for drop-casting films of **SPTE** as a translucent yellowish coatings on glass slides. Diffusion ordered spectroscopy <sup>1</sup>H-(DOSY)-NMR of redissolved samples of thermally treated **SPTE** indicated that polymerisation did not occur to a significant extent (figures S5 and S6). The transmission FTIR spectra of films of **SPTE** containing DMAP or toluene (after heating), dropcast from THF on NaCl slides, showed no difference in the spectra apart from the extra bands corresponding to DMAP (figure S7). Of note is that the ester and spiropyran show strong absorbance relative to the bending modes of the dithiolane moiety. Indeed the strong absorptions of the spiropyran overwhelm the weak bands of the thioctic acid moiety.

## Comparison with model compounds

A deeper understanding of the effect of thermal treatment of **SPTE** can be obtained by comparing with model compounds (figure 3) and especially with the reported polymerisation of thioctic acid.<sup>27</sup> The non-polymerizable octanoic ester (**SP-oct**), thioctic acid (TA) and especially TE, represent various components of **SPTE** and especially the dithiolane unit.

A transition from a crystalline powder to an amorphous film is observed by optical microscopy when **TA** is heated above its melting point, 65 °C (figure S8). Ring opening of the dithiolane to form intermolecular disulfides in linear polymers are described in literature by two different mechanisms, namely radical polymerization<sup>39</sup> and anionic exchange reaction.<sup>35</sup> The ATR-FTIR spectrum of **TA** shows broadening of bands in the fingerprint region of the

heat treated sample compared to the original crystalline sample, which could be ascribed to polymerization (figure S9).

Raman spectroscopy provides further insight into the change in structure of the five membered disulfide ring. In the low wavenumber region, there is a change in band shape, especially the three bands in the  $400\text{ cm}^{-1}$  region. Thioctic ester (**TE**) shows a smaller change in this region, which indicates that polymerization does not occur or that the Raman spectra are different at different extents of crystallinity of the five membered ring structure. When the compound is in a crystalline state, there are sharp Raman bands while broad bands are characteristic of an amorphous state.<sup>42</sup> These data contrast with earlier reports in which the disappearance of these bands was taken as an indication for polymerization.<sup>27</sup> It is likely that polymer disulfides originating from five membered rings would show a disappearance of these bands, but it is not definitive as the changes observed can be induced by a change in morphology of the solid also. Indeed the absence of the dithiolane specific bands at  $400\text{ cm}^{-1}$  in the spectra of the **SPTE** is therefore likely due to differences in crystallinity and that it is not able to form the same crystal structure as TA. Hence, it is not possible to conclude polymerization of the disulfide occurs by Raman spectroscopy.

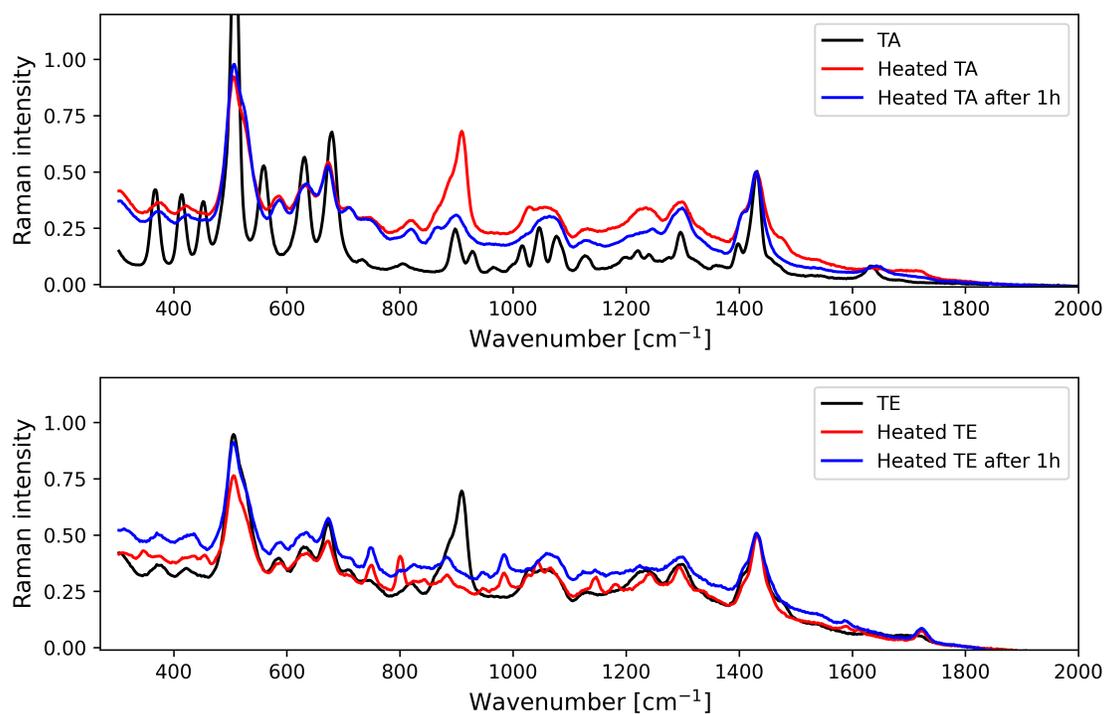


Figure 4: Raman spectra ( $\lambda_{exc}$  785 nm) of **TA** (top) and **TE** (bottom) as solid, after heating, and 1 hour at r.t. after heating, spectra are normalized to the band at  $1430\text{ cm}^{-1}$

## Photochromism of SPTE thin films

The photoswitching of **SPTE** in the solid state both as prepared and after heating to form an amorphous solid was compared with that of **NSP**. The photochemistry of **NSP** is well characterised in solution and dispersed in PMMA,<sup>40</sup> with the appearance of an absorption band in the visible spectrum upon irradiation at 365 nm. Comparison of the spectra of **SPTE** films prepared by drop casting, **NSP** in solution and **NSP** in PMMA films (Figure 5) are broadly similar. The absorption spectrum of **SPTE** films shows a red shift compared to the **NSP** in PMMA and similar in shape and position of the absorption maximum to that of **NSP** and **SPTE** in solution. These data indicate that the polarity in the **SPTE** film is close to that in acetonitrile.<sup>43</sup> Thermal recovery of the spiropyran form following photoswitching is slower than in solution, which is expected due to the lower conformational freedom available to the spiropyran/merocyanine in the film. The relative intensity of the bands at ca. 590 nm and 365 nm are indicative of the extent of conversion since the absorptivity of both the spiropyran and merocyanine isomers of **NSP** are similar at 365 nm (the wavelength of irradiation). The ratio of these bands in the **SPTE** film is lower than for **NSP** in acetonitrile and in PMMA films, indicating a lower extent of conversion, or rather a gradient of conversion through the film.<sup>40</sup>

## Photoswitching of water contact angle

The effect of irradiation of a dropcast thin film of **SPTE** on glass at 365 nm on its surface energy was determined by water contact angle measurements (figure S10). Irradiation results in a decrease in water contact angle by 17.8°, which is consistent with the increase in polarity of the merocyanine isomer with respect to the spiropyran isomer reported in literature,<sup>3,6</sup> and consistent with the change in the UV/Vis absorption (figure 6). It should be noted that *in situ* irradiation with the water droplet on the surface is hampered by the absorption of the water into the film resulting in swelling. Diiodomethane, which dissolved the coating, and n-dodecane both provided a contact angle less than 1°. Furthermore, although UV/vis

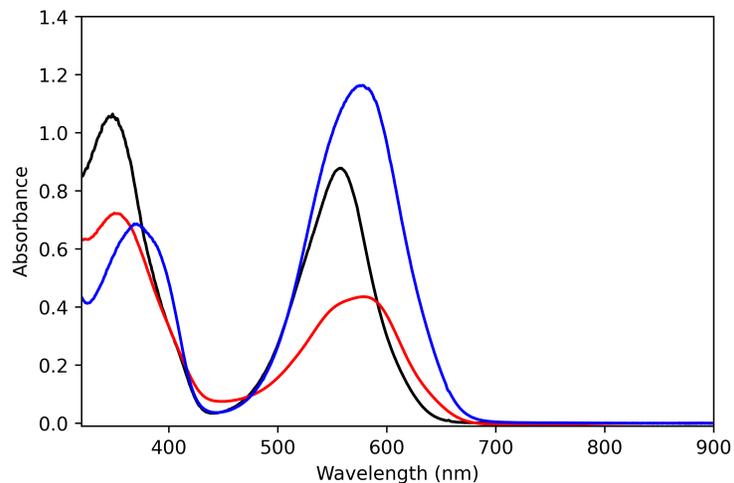


Figure 5: UV/vis absorption spectra of after irradiation at 365 nm; of **NSP**) in acetonitrile (100  $\mu$ M) (blue), **SPTE**) dropcast on a glass slide (red), and **NSP** dispersed with PMMA (spin coated on a glass slide, black).

absorption spectroscopy indicates that the photochromism in the films is reversible, the contact angle does not recover to its original value after irradiation. Hence, the effect of irradiation on the surface of the film, which determines surface energy, is off interest and was investigated further.

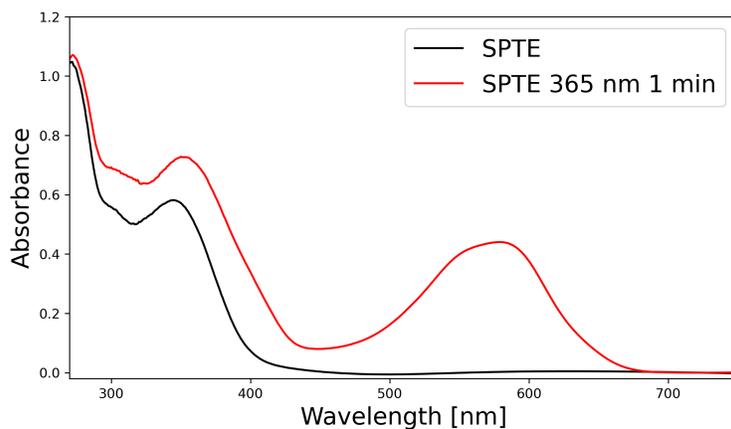


Figure 6: UV/vis absorption spectrum of **SPTE** dropcast on a glass slide before (black) and after (red) irradiation at 365 nm.

## Photochromism at the surface of films of SPTE

Photochromic switching of thin films formed from **SPTE** between spiropyran and merocyanine states can be followed by vibration (Raman and FTIR) spectroscopy. In contrast to transmission techniques where the whole depth of the film is probed (i.e. UV/vis absorption spectroscopy), the confocal nature of Raman spectroscopy means that the top ca. 5 to 10 micron can be probed (i.e. are within the confocal volume). Hence it is a suitable technique for probing changes at the surface of SPTE films. Irradiation of a thin film at 365 nm sees a rapid appearance of Raman bands of the merocyanine form (Figure 7). However, the greater polarisability of the merocyanine isomer means that its spectrum dominates the Raman spectrum and the relative intensities do not reflect directly the relative concentrations of the isomers. It is therefore difficult to distinguish the spiropyran isomer where even a relatively small amount of the merocyanine isomer is present. Subsequent irradiation for 15 min at 565 nm recovers the spectrum of the spiropyran isomer, however, there are several additional bands that cannot be assigned to neither the spiropyran nor the merocyanine isomers, for example at  $1350\text{ cm}^{-1}$ , indicating photodegradation.

Switching was further investigated by diffuse reflectance FTIR (DRIFTS) spectroscopy where heat treated **SPTE** was dissolved in THF and drop cast on a powdered KBr substrate. The absorption spectrum of the **SPTE** changed upon irradiation, however, the spectrum changes were less pronounced compared to those observed by Raman spectroscopy. This limited change could be due to the lower intensity of the light (365 nm) illuminating the sample in the case of the DRIFTS experiment, however, film thickness affects the measurements also due to a primary inner filter effect. This material (**SPTE**) has a strong inner filter effect as both the spiropyran and merocyanine forms absorb similarly at 365 nm and therefore only the top layer of the coating is irradiated with the majority of the material untouched but still contributing to the FTIR absorption spectrum. Nevertheless as with Raman microscopy, the initial changes can be ascribed to formation of the merocyanine form, however, further changes are observed that indicate the formation of other species (degradation). As

the inner filter effect means that only the surface of the film is irradiated then these changes are of relevance for contact angle measurements (*vide supra*).

Although ATR-FTIR spectroscopy probes the bottom of samples with respect to the surface exposed to air and light source for irradiation, it is suitable to probe optically thin films since the thickness of the film needed is in the low micron range and similar to the confocal depth of the Raman microscope. Furthermore, the absorptivity of the bands of the spiropyran and merocyanine forms of **NSP** and **STPE** are similar with the ester carbonyl stretching band of the later acting as a convenient internal reference. Hence ATR-FTIR makes it an appropriate technique to monitor spiropyran to merocyanine switching in films that are thin enough so that the whole depth can be switched, i.e. the thickness is less than required for inner filter effects at 365 nm to contribute. This aspect is important as it is the reactions at the surface of the film that are relevant to observed change in the water contact angle of the spiropyran coated surface.

Thin films of **NSP** and **SPTE** were drop cast on the ATR crystal of the FTIR spectrometer, taking care to ensure that the films were sufficiently thin to avoid primary inner filter effects. Photowitching of the films from the spiropyran to the merocyanine isomer proceed rapidly upon irradiation of the top of the film with UV light (365 nm).

Several, irradiation cycles were performed performed by irradiation at 365 nm for 5 min with subsequent irradiation at 565 nm for 55 min. Changes in the FTIR spectra show switching from the spiropyran isomer to the merocyanine isomer (figure 9). Following the band around 1600-1620  $\text{cm}^{-1}$ , which corresponds to a conjugated alkene stretching mode of the merocyanine form, shows an increase when the film is irradiated at 365 nm (figure 10). A subsequent decrease in the band is observed upon prolonged irradiation, as well as, with multiple cycles of UV and visible irradiation (figure 10 and S11). This indicates that the merocyanine is lost over time due to degradation rather than reversion to the spiropyran form. The changes in the FTIR spectrum following degradation are such that the spiropyran is significantly degraded.

It is interesting to note that whereas UV/Vis absorption, the most widely used technique to follow photochromic switching, indicates that thin films of SPTE can be switched reversibly over multiple cycles, ATR-FTIR and Raman spectroscopy show that the degradation at the surface of the film is rapid. The results obtained with the latter techniques are therefore of more relevance to understand the switching of surface properties, e.g. changes in water contact angle.

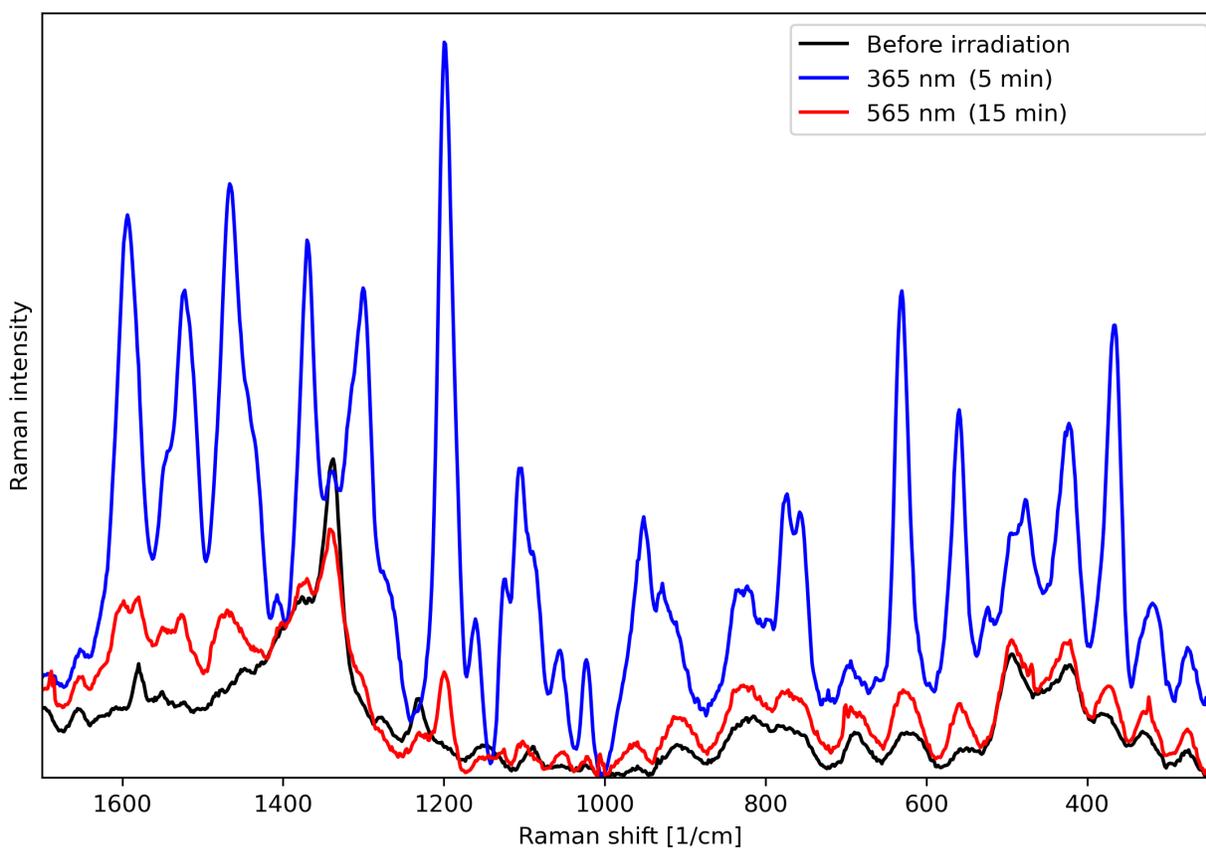


Figure 7: Raman spectrum of a thin of **SPTE** dropcast on a gold coated glass slide from a solution in THF (black) and after irradiation at 365 nm (blue) and an subsequent irradiation at 565 nm.

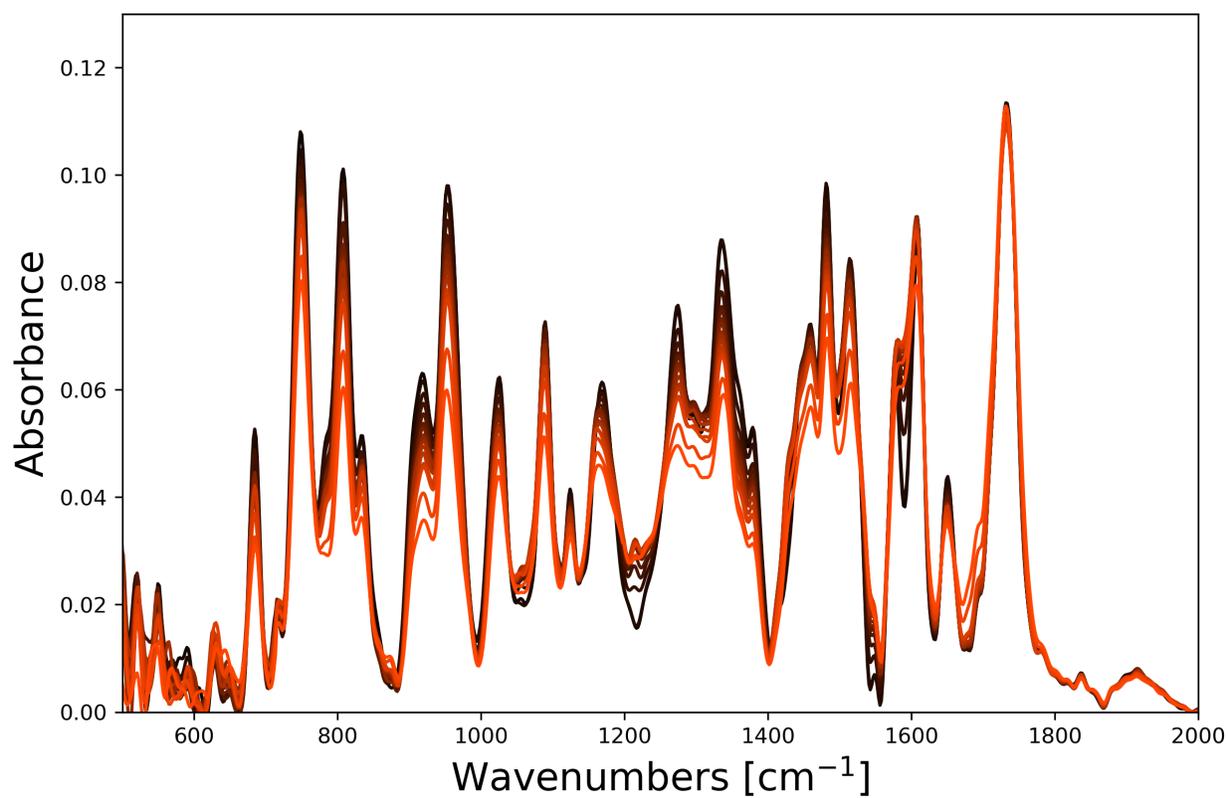


Figure 8: DRIFTS spectra of **SPTE** dropcast from THF on KBr powder before and during irradiation at 365 nm.

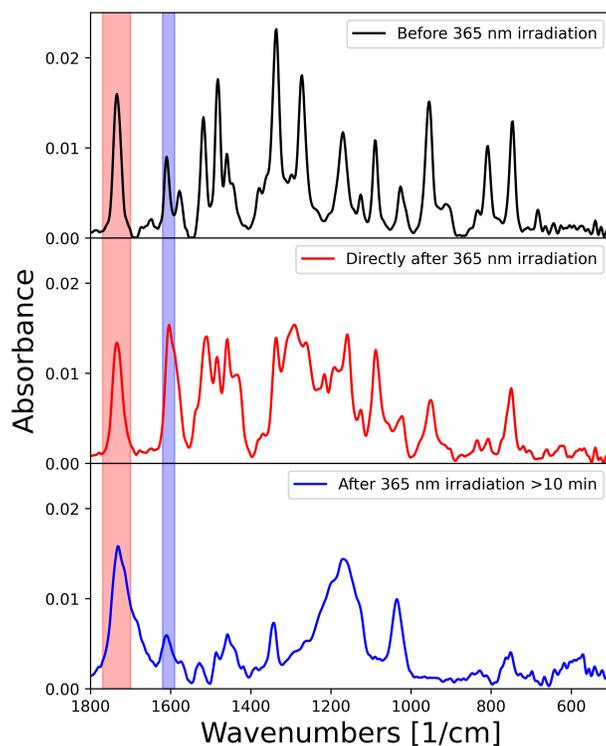


Figure 9: ATR-FTIR spectra of a film of **SPTE** dropcast from THF before (top), during (middle), and after irradiation for an extended period (bottom) at 365 nm.

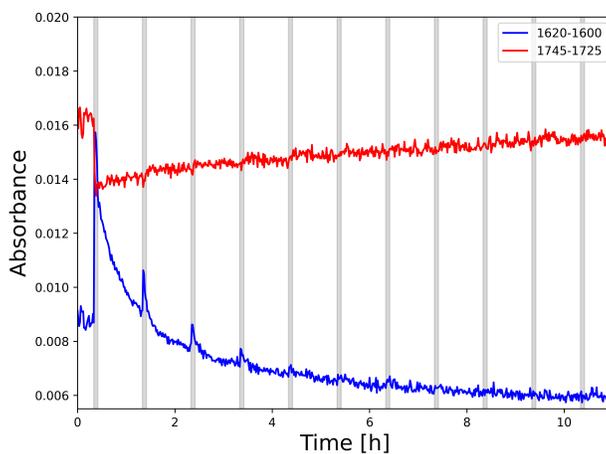


Figure 10: Absorbance (ATR-FTIR) over time at 1620-1600 and 1745-1725  $\text{cm}^{-1}$  of **SPTE**, dropcast from THF, during alternating irradiation with 365 nm (grey line) and 565 nm (white gap).

## Origin of degradation of spiropyrans in thin films

The lack of reversibility in photochemical switching can be ascribed to any of several pathways of degradation (figure 11). The aggregation of the merocyanine form, proposed to occur in solution, should also occur in thin films.<sup>22,23</sup> The expected changes to the UV/vis absorption and FTIR spectra (figure 9) upon switching between the **SPTE** before and directly after irradiation to form the merocyanine isomer are observed and hence, although by definition a thin film of SPTE is aggregated, the merocyanine isomer formed upon irradiation with UV light does not show changes in its spectra typical of significant electronic interactions between molecules in the film. Hence, aggregation of the merocyanine isomer is not the cause of the degradation observed. Degradation due to reaction of the dithiolane

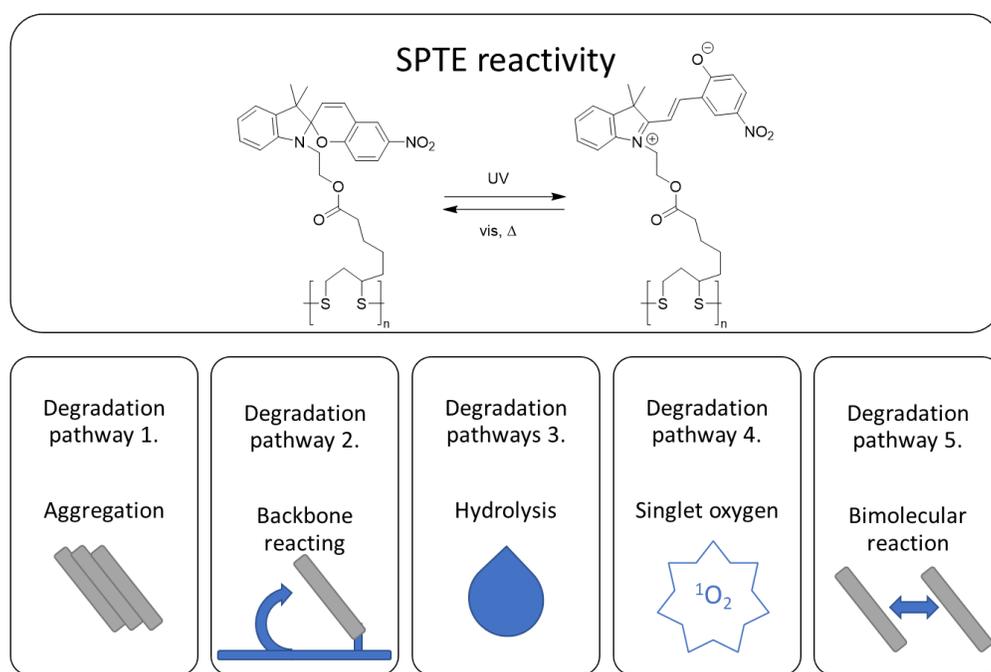


Figure 11: Degradation pathways to be considered of a film of **SPTE**

groups of **SPTE** with the spiropyran isomer can be excluded as the compounds and formed films also switch several days after casting days, which excludes the reaction of the polymer backbone with the spiropyran over this time period. The merocyanine form, however, is an electrophile, especially the central  $\alpha$ ,  $\beta$  unsaturated imine. However, the stability of films

of **NSP**, drop cast on an ATR crystal, under irradiation is similar to that observed with **SPTE** (figure S11), which confirms that the degradation involves the merocyanine isomer alone and not a reaction with the dithiolane moiety. Furthermore, it is highly unlikely that ester hydrolysis occurs over the time scale of the measurements, as the ester C=O stretch is not depleted after 11 h of photochemical cycling while most of the spiropyran/merocyanine absorption bands are lost, i.e. the switching unit has fully degraded.

Singlet oxygen ( $^1\text{O}_2$ ) is a likely source of degradation in this system due to its formation during deactivation of the triplet excited state that the merocyanine is formed in initially from the spiropyran upon photoswitching.<sup>40,44,45</sup> Especially since dropcast **NSP** on the ATR crystal showed similar degradation over the same time as **SPTE**. The potential role of  $^1\text{O}_2$  was examined by irradiation at 365 nm of dropcast thin films of **SPTE** on an ATR crystal followed by FTIR spectroscopy. The rate of loss of absorbance of the merocyanine form was the same under air and under a nitrogen atmosphere (figure 12). Two spiropyran

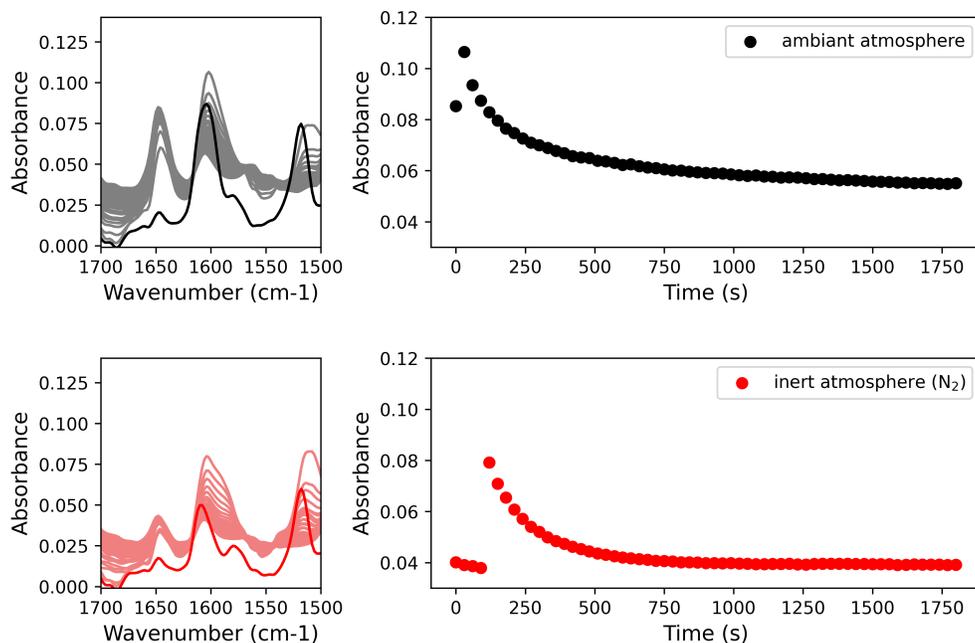


Figure 12: Absorbance of the conjugated alkene stretch at  $1602\text{ cm}^{-1}$  of heat treated **SPTE** under ambient atmosphere (top) and nitrogen atmosphere (bottom) during irradiation at 365 nm.

molecules either both in the merocyanine form or one in the spiropyran isomer and one in

the merocyanine isomer could react with each other. There is one report of such a reaction where it was speculated to be due to this degradation path, albeit without experimental evidence.<sup>46–49</sup> Degradation by a bimolecular reaction of two switches at high concentration, *i.e.* in this system, is likely. This results also in a degradation product protecting the deeper lying molecules from switching and degradation.

## Conclusion

Irradiation of a coating of **SPTE** at 365 nm results in a change in contact angle of 17.8°. However, degradation occurs with continued irradiation, which is readily apparent in ATR FTIR spectra (surface sensitive). Thicker films show negligible degradation as the primary inner filter effects, due to the absorption of the spiropyran/merocyanine, prevents penetration of light. This difference is the origin of the discrepancy in regard to stability when observed by ATR-FTIR and UV/vis absorption spectroscopy. Transmission mode measurements and techniques such as UV/Vis absorption spectroscopy show the properties of the bulk material instead of the material at the surface (relevant for contact angle measurements), which needs to be taken into account when carrying out degradation studies and switching cycles of spiropyran and other switches. It is important therefore to use techniques that are suitable to address the component of the material of interest, in this case the surface. Diffuse reflectance FTIR and Raman spectroscopy show some degradation, but ATR-FTIR spectroscopy proves exceptionally useful for studying changes in thin films relevant for surface studies.<sup>50</sup> In the present study, the facile formation of polymers from thioctic acid is not observed but it is clear that even were polymers to form, photodegradation at the surface is limiting and is intrinsic to the switching process.

## Experimental

All chemicals were purchased from Sigma-Aldrich or TCI chemicals. **NSP** and **SPTE** were prepared as reported by Ivashenko *et al.*<sup>25</sup> All solvents used were of technical grade unless stated otherwise. UV/vis absorption spectra were recorded using a fibre coupled Avantes AVASpec-uls2048cl-EVO-RS or AvaSpec-3648 fibre optic spectrometer with a Avalight DHc or a Ocean optics light source or a Specord 210 UV/Vis absorption spectrometer (AnalytikJena). Electrochemical measurements were performed using a Model 630B or 760C Electrochemical Workstation (CH Instruments). Raman spectra at 785 nm were recorded on using 50x long working distance objective on a BX-51 microscope. Excitation was provided by an ONDAX LM-785 laser (75 mW at source) which was passed through a laser line clean up filter (Semrock LL01-785), a  $\frac{\lambda}{2}$  retarder and polarising beamsplitter to control power followed by a second  $\frac{\lambda}{2}$  retarder to control polarisation. The laser was combined with the optical path of the spectrometer with a dichroic mirror (45°) (Semrock Di02-R785) and directed to the microscope with gold mirrors. The Raman scattering passed through the dichroic mirror and a Rayleigh line rejection filter (Semrock BLP01-785R) and was focused with a 35 mm focal length plano convex lens into an Andor Kymera-193i spectrograph with a 600 l/mm grating blazed at 750 nm and Andor idus-DU416A-LDC-DD CCD camera. Spectra were acquired with Andor Solis. Spectra were calibrated with polystyrene or cyclohexane (ASTM E 1840). FTIR spectra were recorded on a PE Spectrum 2 with ATR attachment. Irradiation was carried out using mounted LEDs (365 nm (4.1 mW, M365F1, Thorlabs) and 565 nm (2.0 mW, M565F1, Thorlabs).

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## ASSOCIATED CONTENT

Supporting Information. Additional Raman spectroscopic data are provided as Supporting Information.

## Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

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