

Opening the way to greener photochromic and fluorescence studies by using the 6-NO₂-BIPS photoswitch

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Abstract. This article investigates the photochromic and fluorescence response of the spiropyran-derived 6-NO₂-BIPS photochrome in different media using a green chemistry approach. A red fluorescence emission of the coloured form was observed in all the tested media. The spontaneous back-reaction of the UV-irradiated compound was studied by absorption spectroscopy in 2-Me-THF [$t(1/2) = 19.7$ s], cyclopentyl methyl ether (CPME) [$t(1/2) = 12.6$ s] and a water/ethanol/SDS solution [$t(1/2) = 146$ min]. The latter was found to enable quasi-P type photochrome behavior. Drop-casted and spin-coated thermoplastic polyurethane films were prepared at 1 and 2 mass percentages of 6-NO₂-BIPS as a dopant. The films could offer promising results, especially in applications mimicking photochromic glass behavior.

Keywords: Photochromism / fluorescence / green chemistry

1 Introduction

Amongst molecular switches, such as dithienyl-ethenes and azobenzenes, spiropyrans have inspired the scientific community to conduct research on their properties for over a century now [1,2]. Part of the interest comes from their responsiveness to a wide range of stimuli such as temperature changes, solvent polarity, and light irradiation. Part of this class of compounds exhibits a singular response to light-triggered processes: photochromism. Such photochromic compounds possess the ability to change colors and therefore optical properties upon irradiation at given wavelengths of interest. Once in irradiated form, photoswitches are known [1] to reverse back to their original form in two possible ways: thermally (T-type photochromism) or photochemically (P-type photochromism). These compounds have gained popularity due to their possible applications in a variety of fields like energy storage [3], eye-protection glasses [4], and several others [5–7].

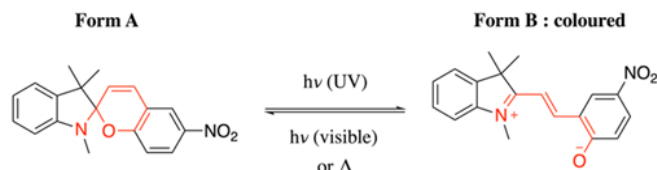
6-nitro-2-(1H-imidazol-1-yl)phenol (6-NO₂-BIPS) is a photoswitch belonging to the spiropyran family. Upon irradiation with UV light, the colourless spiropyran A form undergoes a ring-opening isomerization to produce the coloured merocyanine B form, and spontaneously goes back to the closed-ring form (Scheme 1). This compound has been largely studied [8–11] mainly for its distinct solvatochromic, photochromic and fluorescence properties

over the past few years. The color of the B form was found to be highly affected by the polarity of the solvent in which it dissolves [8].

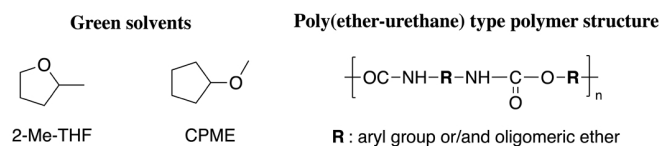
The series of experiments presented in this article sets out to investigate the photochromic behavior and photophysical properties of 6-NO₂-BIPS whilst adopting a green chemistry approach. This involves developing processes and syntheses that reduce or eliminate the use and production of harmful substances. The principles of green chemistry [12], allow the use of renewable feedstocks as much as possible, thus limiting the production and use of reagents from petrochemicals, which are major contributors to the climate impact of fine-chemical industries [13]. The photoswitch was chosen to be studied in the three following solvents providing different polarity media: cyclopentyl methyl ether (CPME) [13], 2-methyltetrahydrofuran (2-Me-THF) [14] and water, which is the most bio-sourced one [15].

However, due to solubilization problems, a sodium dodecyl sulfate (SDS) surfactant and 10 percent ratio ethanol (co-solvent) were added to water and formed a soluble mixture (WES). In solution, the first-order kinetics of the thermal back-reaction (form B to form A) were analyzed, and the photochromic and fluorescence properties were characterized by absorption and fluorescence spectroscopy. In addition, the compound was dispersed in an aromatic polyether-based thermo-plastic polyurethane matrix (Scheme 2), showing perspectives for recycling

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Scheme 1. Isomerization reaction of 6-NO₂-BIPS.



Scheme 2. Green solvents used and general structure of a poly(ether-urethane)-type polymer.

[16,17], so that the effect of structure on its photophysical properties could be further studied by absorption and fluorescence.

2 Materials and methods

The 6-NO₂-BIPS compound (1',3'-Dihydro-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole], 98%) was purchased from Sigma-Aldrich and used for all the conducted experiments.

The cyclopentyl methyl ether (CPME, $\geq 99\%$) and 2-methyltetrahydrofuran (2-Me-THF, $\geq 99\%$) are EMPLURA® grade solvents. These solvents and the sodium dodecyl sulfate surfactant (SDS, $\geq 99\%$) were also purchased from Sigma-Aldrich and used without further purification. The ethanol utilized in this study was a generic laboratory-grade reagent ($\geq 95\%$).

2.1 Polymer film preparation, 2% (DC-2) doping

1.13 g of thermoplastic polyurethane @Pearlstick polymer (TPU) beads (Pearlstick™ 5714 F1 provided by Lubrizol Advanced Materials) were dissolved in 20 mL of 2-Me-THF under stirring in an Erlenmeyer flask equipped with a cooler at 70°C for 2 h. 23.6 mg of 6-NO₂-BIPS were then added to the mixture and left under stirring for 15 additional minutes: a 2% in mass doped homogeneous polymer solution was obtained.

The polymer solution was then quickly poured in a petri dish placed on a hot plate at 70°C which was immediately covered with a crystallizer. The crystallizer was regularly wiped of the 2-Me-THF condensate. Once the solvent condensation stopped, the film was heated at 100°C for 5 min before melting; the hot plate was then turned off. The film was left to return to room temperature.

2.2 Spin coated film, 1% (SC-1) doping

The doped solution was prepared following the protocol mentioned above starting from 1.1 g of polymer beads dissolved in 15 mL of 2-Me-THF in order to obtain more viscous solutions (Table 1), which are deemed to be

preferable for spin-coating. The doping percentage of the film was obtained by adding 11,8 mg of the doping compound to the polymer solution described above. Dynamic depositions of 30 μ L of the polymer solution were performed in the first 5 s of the scheduled time on a glass slides rotating on the disk of an Ossila Spin Coater (L2001A3-E461-UK). After several trials, the parameters producing the most optimal results were: 180 s rotating time at 2000 rpm.

2.3 Solution preparation

0.4 mM 6-NO₂-BIPS solutions were prepared in CPME and 2-Me-THF. An additional 0.4 mM 6-NO₂-BIPS solution was obtained by firstly dissolving the compound in ethanol and then adding it to a water/surfactant mixture. The resulting water/ethanol/surfactant (WES) solution comprises a volumetric mixture consisting of 10% ethanol and 90% water, with the SDS surfactant incorporated at a concentration of 0.32 M within the overall ethanol/water blend.

2.4 Sample analysis

The absorption spectra and kinetics of the various solutions were recorded using a Biochrom Libra S12 spectrophotometer using 1 cm path length quartz cuvettes. The emission spectra were recorded using the Cary Eclipse fluorimeter. The absorption spectra of the polymer films were recorded with a Xenius Safas Monaco spectrophotometer and their emission spectra with a Safas Xenius XC spectrofluorometer. The irradiation of the solutions and the films was performed using a Vilber Lourmat 6-Watt UV lamp.

3 Results and discussion

3.1 Absorbance and kinetics in solution

The absorption spectra of the photochrome in 2-Me-THF were measured before and after irradiation with a UV-365nm lamp showing the absorbance properties of the A and B form (Fig. 1). The spectra significantly overlapped in the UV range, suggesting an equilibrium between the two isomers. After a 1-min exposure to 365 nm irradiation, the spectral band characterizing this equilibrium remained unchanged, confirming the establishment of a photostationary state (PSS) between the A and B forms. In the visible range, the non-irradiated sample did not absorb while the irradiated sample did ($\lambda_{\text{max}} = 58$ nm) (Table 1). Consequently, the appearance of a band in the visible region characterized the presence of B form in solution. This observation further implies that a fraction of the A form photochemically converted to the B form.

A similar behavior was observed for the samples of 6-NO₂-BIPS in CPME (Fig. 2, $\lambda_{\text{max}} = 575$ nm) and in WES (Fig. 3, $\lambda_{\text{max}} = 525$ nm). According to Table 1, the polarity of the solvents increases as follows: CPME, 2-Me-THF, THF and WES. The anticipated negative-solvatochromic effect, as reported in the literature for

Table 1. Summary of results of kinetics, absorption and fluorescence spectra for the B form of the 6-NO₂-BIPS in different polarity environments; (a) all data provided for THF originates from [8]; (b) the ethanol/water mixture ε (without taking into account the SDS) can be approximated by using data provided in [18]; (c) no values found in the literature; (d) values not measured; (e) stands for the maximum wavelength in absorption in the visible range; (f) maximum wavelength in fluorescence emission

Solvent	Dielectric constant ε	Dipolar moment μ (Debye)	$\lambda_{\max, \text{abs}}^{(e)}$ (B form) (nm)	$\lambda_{\max, \text{fluo}}^{(f)}$ (B form) (nm)	Thermal back reaction half-life $t(1/2)$ (s)	Thermal back reaction constant $k(s^{-1})$
CPME	4.76	1.27 (calc)	575	639	12.6	$5.5 \cdot 10^{-2} \pm 9.0 \cdot 10^{-4}$
2-Me-THF	6.77	1.38	585	659	19.7	$3.5 \cdot 10^{-2} \pm 7.4 \cdot 10^{-5}$
THF ^(a)	7.58	1.75	583	(-) ^(c)	20.8	$3.3 \cdot 10^{-2}$
WES	50 ^(b)	(-) ^(c)	525	625	$8.76 \cdot 10^3$	$7.9 \cdot 10^{-5} \pm 2.8 \cdot 10^{-7}$
SC-1	(-) ^(c)	(-) ^(c)	562	638	(-) ^(d)	(-) ^(d)
DC-2	(-) ^(c)	(-) ^(c)	561	625	(-) ^(d)	(-) ^(d)

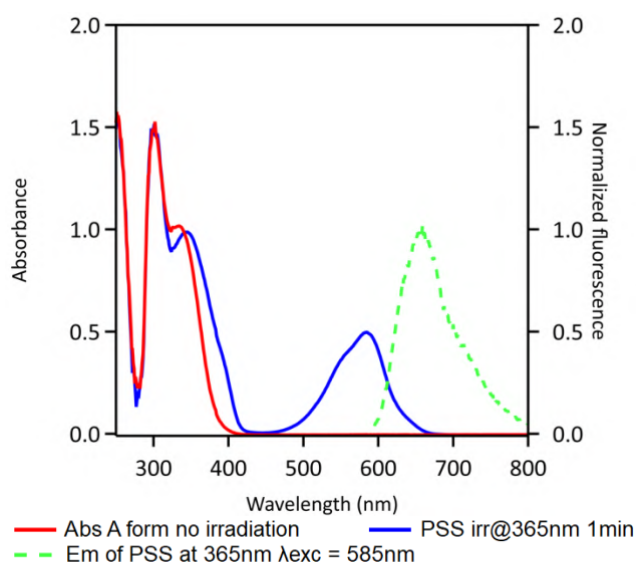


Fig. 1. Absorbance spectra (non-irradiated sample and 365 nm PSS reached upon 1 min of irradiation) and normalized fluorescence emission spectrum (recorded at 585 nm excitation of the 365 nm PSS) of BIPS in 2-Me-THF (0.4 mM).

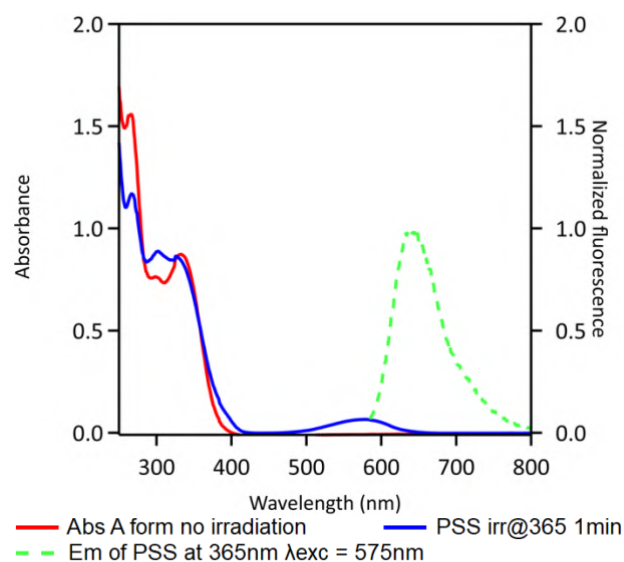


Fig. 2. Absorbance spectra (non-irradiated sample and 365 nm PSS reached upon 1 min of irradiation) and normalized fluorescence emission spectrum (recorded at 575 nm excitation of the 365 nm PSS) of BIPS in CPME (0.4 mM).

6-NO₂-BIPS, suggests a decrease in $\lambda_{\max, \text{abs}}$ (B form) with increased solvent polarity [8], [10]. However, despite observing a general hypsochromic effect in this study [$\lambda_{\max, \text{abs}, 2\text{-Me-THF}}$ (585 nm) $\approx$ $\lambda_{\max, \text{abs}, \text{THF}}$ (583 nm) $>$ $\lambda_{\max, \text{abs}, \text{WES}}$ (525 nm)], CPME ($\lambda_{\max, \text{abs}, \text{CPME}}$ = 575 nm) was an exception.

The fact that $\lambda_{\max, \text{abs}}(\text{B form})_{\text{CPME}} < \lambda_{\max, \text{abs}}(\text{B form})_{\text{THF}}$ could indicate that in CPME, compared to THF, the ground-state is better stabilized than the excited state by solvation (Scheme 3).

In contrast to observations in CPME and 2-Me-THF, the WES solution exhibited a minor visible range band prior to UV irradiation, indicating a pre-existing conversion of a fraction of A form to B (Fig. 3). This may result from the samples not being prepared under dark conditions. Indeed, visible light energy might have been adequate to induce photoisomerization. This observation gains further clarity when considering the subsequently

examined higher thermostability of the B form in WES, providing an additional explanation for its presence before irradiation.

Being spontaneous and occurring thermally, the ring-closing back-reaction (Scheme 1) was convenient to monitor in absorbance after subjecting the photochrome to a 365 nm UV-lamp irradiation for a few minutes at 20°C (Fig. 4). The kinetic study in 2-Me-THF, showed a first-order mechanism in the back ring-closing reaction ($\chi^2 = 1.9 \cdot 10^{-4}$) (Fig. 4a). The half-time and rate constant of the reaction (Table 1) were calculated by fitting the $A_{585\text{nm}} = f(t)$ data with an exponential (Fig. 4a). These results are extremely similar to the ones found in THF (Tab. 1). Hence, 2-Me-THF may prove to be a suitable substitute to regular THF for the study of the photochromic properties of the compound. Likewise, the kinetics of the photochrome in CPME showed first-order kinetics ($\chi^2 = 9.2 \cdot 10^{-5}$), Fig. 4b) but faster ($t_{1/2} = 12.6$ s

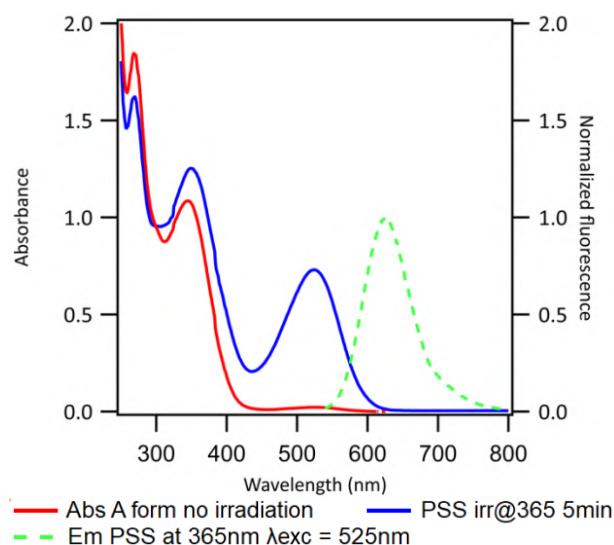
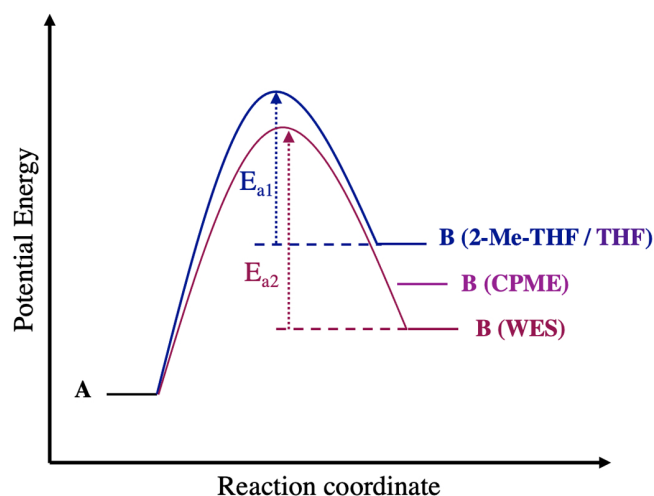


Fig. 3. Absorbance spectra (non-irradiated sample and 365 nm PSS reached upon 5 min of irradiation) and normalized fluorescence emission spectrum (recorded at 525 nm excitation of the 365 nm PSS) of BIPS in WES (0.4 mM).



Scheme 3. Proposed potential energy diagram of the 6-NO₂-BIPS isomerization reaction carried out in different solvents **3**.

and $k = 5.5 \cdot 10^{-2} \pm 9.0 \cdot 10^{-4} \text{ s}^{-1}$) compared to 2-Me-THF ($t_{1/2} = 19.7 \text{ s}$ and $k = 3.5 \cdot 10^{-2} \pm 7.4 \cdot 10^{-5} \text{ s}^{-1}$). The detail of the calculations made is presented in *Appendix A*.

The kinetics of 6-NO₂-BIPS in WES showed a slight decrease in absorbance for $t < 300 \text{ min}$, then a constant non-zero absorbance persisted indicating that the merocyanine form is highly stable in this mixture (Fig. 4c). This stability could arise from the capacity of the alkoxy group in the B form to form hydrogen bonds with the highly protic WES.

However, when carried out photochemically, the back-reaction occurs even if the discoloration appeared more slowly to the naked eye than for the other analyzed solutions (CPME, 2-Me-THF) for which the photochemical reaction occurred in a few tens of seconds (*Appendix B*).

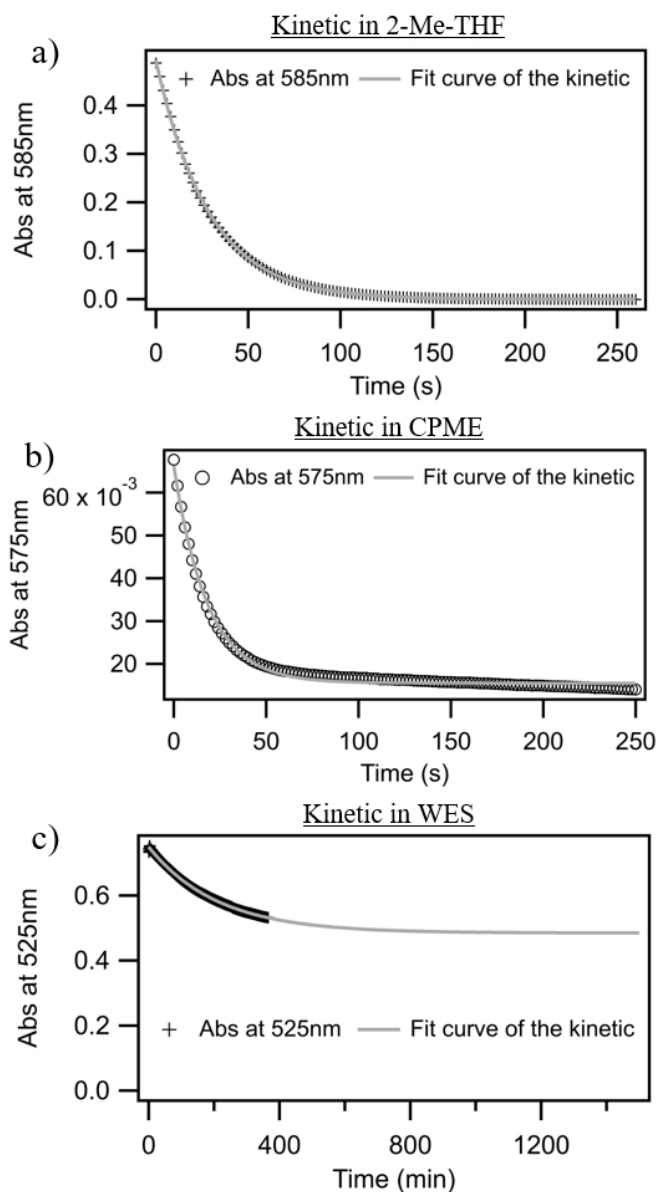


Fig. 4. Fitted kinetic curves of the ring closure reaction (B to A form) followed in absorbance of BIPS at 585 nm, 575 nm, and 525 nm in respectively 2-Me-THF(a), CPME (b) and WES (c) ([BIPS] = 0.4 mM). The absorbance at $t = 0 \text{ min}$ corresponds to the PSS reached upon 365 nm irradiation in each respective solvent.)

The properties of 6-NO₂-BIPS in WES could therefore be regarded as those of a quasi-P type photochrome whereas in CPME and 2-Me-THF, the compound behaved as a T-type photochrome.

3.2 Fluorescence

The metastable B form of 6-NO₂-BIPS is known to exhibit fluorescent properties upon excitation within its characteristic visible range absorption band [8]. Upon exciting the 365 nm PSS at the respective $\lambda_{max,abs}$ (B form), fluorescence was consistently observed across all prepared solutions (Figs. 1, 2 and 3. Distinct yet

closely situated emission bands were identified for CPME ($\lambda_{\text{max, fluo}} = 639 \text{ nm}$), 2-Me-THF ($\lambda_{\text{max, fluo}} = 659 \text{ nm}$) and WES ($\lambda_{\text{max, fluo}} = 625 \text{ nm}$), with summarized results presented in Table 1. All emission spectra exhibited a red-shift relative to their respective absorption bands.

The magnitude of this red-shift, quantified as the Stokes shift ($\Delta\sigma$), where $\Delta\sigma = \sigma_{\text{max, abs}} - \sigma_{\text{max, em}}$, revealed significant differences among solvents. According to the Franck-Condon principle, the two electronic states involved in the $S_1(v'=0) \rightarrow S_0(v''=0)$ transition displayed the largest difference in equilibrium geometries in WES ($\Delta\sigma = 3048 \text{ cm}^{-1}$) compared to 2-Me-THF ($\Delta\sigma = 1920 \text{ cm}^{-1}$) and CPME ($\Delta\sigma = 1742 \text{ cm}^{-1}$). These variations could be attributed to solvation effects, suggesting that as solution polarity increases, the energy of the electronic transition between the excited and ground state of 6-NO₂-BIPS (B form) also rises.

Furthermore, in comparison to the other solvents, the protic character of WES, as previously indicated, may play a crucial role in stabilizing the ground state of B relative to its excited state. This observation provides a plausible explanation for the larger exhibited $\Delta\sigma$ in WES.

These properties of the photoswitch, coupled with its fluorescence characteristics, hold significant potential for applications in chemo-sensing and imaging [11].

3.3 Photophysical behavior in a TPU polymer matrix

Two doped samples were obtained at different percentages in mass: a 1% doped spin-coated film (**SC-1**, Fig. 5) and a 2% drop-casted film (**DC-2**, Fig. 5). The two doping percentages were chosen under 5% in order to mitigate potential inner-filter effect that might alter switching efficiency of 6-NO₂-BIPS within the polymeric samples. Under visible light, at room temperature, the A form of the dispersed compound was predominant: the two films appeared transparent to the naked eye (Fig. 5). In the absorption spectrum of **SC-1A** (red line, Fig. 6), no band was present in the range of visible light. In the absorption spectrum of **DC-2A** (red line, Fig. 7) a weakly absorbing band could be noticed at 561 nm, indicating a minor presence of the merocyanine form. As described in the literature [6], at room temperature, an equilibrium was reached between the spiropyran /merocyanine couple.

Upon UV-irradiation, the B form ratio in the samples increases: **SC-1** and **DC-2** undergo a distinctly noticeable violet photo-coloration (Fig. 5). The absorption spectra of **SC-1** and **DC-2** taken right after 1 min irradiation at 365nm (blue lines, Figs. 6 and 7) show a considerable increase of the 561 nm (**SC-1**)/562 nm (**DC-2**) absorption band that is consistent with the observed change in color.

After removal of the UV light, the enhanced violet coloration slowly reverts back to the original transparent one. The back-reaction has been observed to occur photochemically under visible light (Appendix C).

The B form is known to exhibit a hypsochromic shift in absorption band as the polarity of the solvent increases [8]. Given the similarity in position and shape of the absorption band of the B form of **DC-2** (561 nm) and **SC-1**

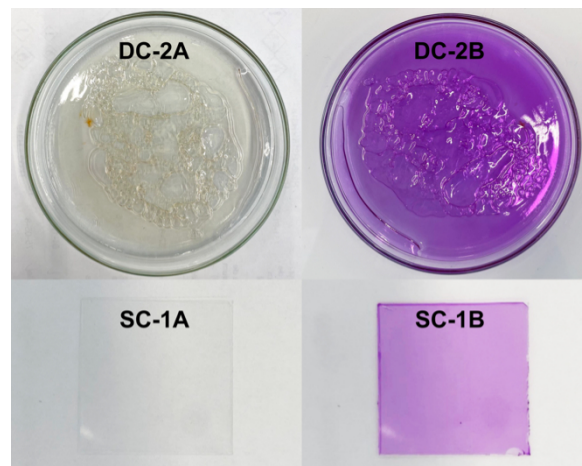


Fig. 5. (Top images) The drop-casted 2% doped TPU Pearlstick in a petri dish. (Bottom images) The spin-coated 1% doped TPU Pearlstick on a glass specimen (Left: before UV irradiation, Right: after 1 min 365 nm UV irradiation.).

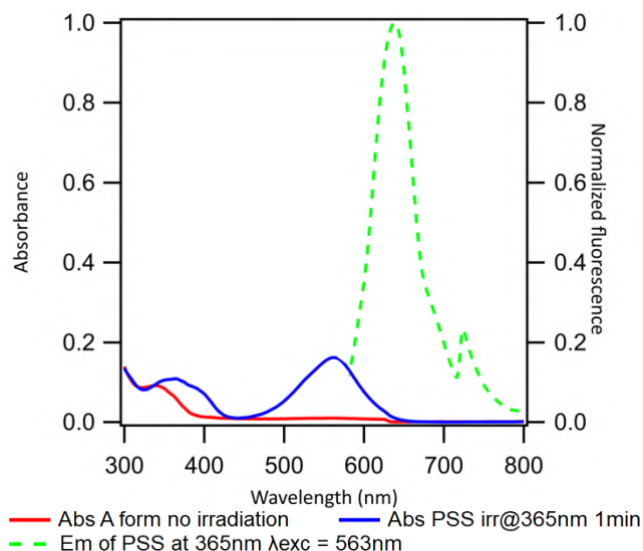


Fig. 6. Absorbance and normalized fluorescence spectra of the non-irradiated and 365 nm irradiated SC-1 doped polymer spin-coated on a glass specimen; the band recorded at 720 nm in the fluorescence spectrum is due to an instrumental artifact.).

(562nm), it can be assumed that the dye molecules were in the same environment in the two samples. Moreover, the bands were located $23.5 \pm 0.5 \text{ nm}$ ($715 \pm 16 \text{ cm}^{-1}$) lower in absorption than the 2-Me-THF ones, which suggests that the polymer matrix created a medium that is much polar than the initial dissolving 2-Me-THF solvent, without altering its photochromic properties.

The red fluorescence of the B form observed in the 2-Me-THF solution (Fig. 1) persisted in the two polymer samples (green line, Figs. 6 and 7). However, there was a 13 nm (326 cm^{-1}) red-shift in the position of the emission band of **SC-1** (638 nm) compared to **DC-2** (625 nm) (Tab. 1). This shift could be due to medium

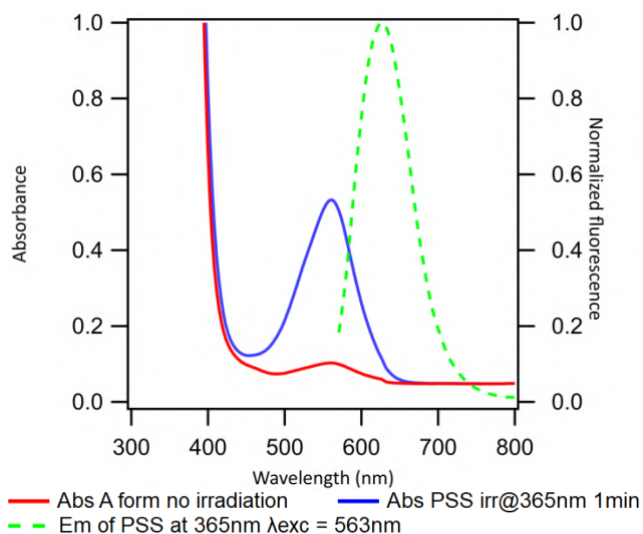


Fig. 7. Absorbance and fluorescence spectra of the non-irradiated and 365 nm irradiated DC-2 doped polymer drop-casted in a petri dish.).

effects as the deposition techniques of the two samples led to coatings varying in thickness and possibly influenced the assembly of polymer-chains in the matrix. Conducting fluorescence decays experiments on the samples could provide an explanation for the effects causing the observed shift.

4 Dead end

Unexpected results were obtained when conducting the set of experiments. Firstly, the multitude of attempts to dissolve the 6-NO₂-BIPS in water-surfactant mixtures in various ratios did not lead to a complete dissolution of the compound. Adding ethanol to the mixture was necessary in order to obtain a homogeneous solution. Secondly, the B form was unexpectedly stable in WES. This led to a considerably slow ring-closing thermal isomerization, which made it difficult to monitor the reaction rate in absorption spectroscopy. Drawing conclusions from the experiment was therefore challenging. The kinetic study was performed overnight and the next day the solution in the cuvette was still pink-colored. The B form of this solution was found to convert back to the A form primarily by photochemically induced isomerization. Finally, even when using the same parameters, the spin-coating procedure required several trials in order to secure uniformly coated films. This reproducibility problem arises from the fact that spin-coating can be highly operator-dependent [19].

5 Conclusion

In summary, the investigation into the photophysical properties of the 6-NO₂-BIPS photoswitch within two green solvents, namely 2-Me-THF and CPME, revealed a first-order ring-closing thermal isomerization reaction,

providing fundamental insights into kinetics. Notably, the enhanced stability of the colored form in WES suggests intriguing possibilities, warranting exploration of proticity effects on the thermal stability of the merocyanine form.

Formulating the photoswitch in a thermoplastic polyurethane matrix yielded spin-cast and drop-cast films, showcasing a sharp photochromic response. However, further assessments of film resistance to fatigue and kinetics of isomerization reactions are pending, holding promise for applications ranging from cost-effective manufacturing variants mimicking photochromic glass behavior to UV-light detection probes.

Determining the 365 nm PSS ratio of B to A form in different solvents would be instrumental. These insights will not only enhance our comprehension of the solvent-dependent efficiency of the photo-isomerization process but will also contribute to discerning the potential influence of solvent on the fluorescence properties of the B form.

These solution-based investigations contribute to expanding our understanding of the 6-NO₂-BIPS photo-switch and spiropyran-based photoswitches. The insights gained open avenues for potential applications in optoelectronic devices and materials, highlighting the ongoing evolution of photoresponsive materials for technological advancement.

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Supplementary material

Supplementary information on the calculations used in order to obtain Table 1 and on the photochemical back-reaction can be accessed via the following database: https://drive.google.com/drive/folders/1TbJvV0hBXUel3u-SiE_Cp-1BY1rSQg0h?usp=sharing.

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