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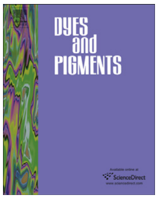

# Diversely halogenated spiropyrans - Useful synthetic building blocks for a versatile class of molecular switches

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## ABSTRACT

Spiropyrans are dyes that can be reversibly switched to a highly colored merocyanine form by a number of stimuli such as light, mechanical force or temperature. To make use of these molecules, there is a requirement to functionalize them appropriately. Herein we report a library of spiropyrans bearing two (pseudo) halide functional groups on either half of the molecule. Such halide substituents are valuable, because they themselves may be used as reactive sites in cross-coupling reactions, for example. Different combinations of halides, for which different reactivities in cross-coupling reactions may be expected, will facilitate selective consecutive cross-coupling reactions and condensations. Data concerning the UV/vis characteristics, the photostationary equilibria of the materials as well as the half-life of the merocyanine forms in solution are presented.

## 1. Introduction

Molecular switches are molecules that can exist in two or more metastable states. They can be transformed from one state into the other by applying external stimuli such as changes in pH, irradiation with light or by mechanical force [1–3]. Molecular switches are therefore instrumental for the development of new "intelligent" materials, [4] or molecular machines [5]. Spiropyrans belong to the most important molecular switches, because of the exceptionally large variety of diverse stimuli that can be used for switching: Their isomerization between a closed spiropyran form and an open merocyanine form can be induced by light, [6] pH, [7–10] the presence of ions, [11–13] pressure, [14] mechanical force [1,2,14–21] as well as electric fields [19,22]. Of those stimuli, the light induced switching provides to be easily accessible and nondestructive. In addition, the absorption coefficient for the merocyanine forms is extremely high (ca. 45,000 L mol$^{-1}$ cm$^{-1}$ at 550 nm) [23] so that only very low concentrations of switches have to be present to detect switching events visually (Fig. 1).

The photochemical properties of the open merocyanine form, with its closed ring systems connected by an sp3 carbon centre, are in striking contrast to the properties of the spiropyran.

Whereas spiropyrans consist of two separated $\pi$-electron systems and therefore absorb only in the UV region of the spectrum, merocyanines possess one planar $\pi$-system. In this $\pi$-system, the electrons are delocalized across the entire molecule, which causes a broad absorption maximum at ca. 550 nm. Irradiation with light of wavelengths that correspond to the absorption maxima leads to a decrease in the concentration of the irradiated species. Therefore, UV irradiation induces the ring opening, whereas visible light facilitates the ring closure (Fig. 1).

Since 2007, spiropyrans have been used as mechanophores [6]. Therefore, they represent a relatively rare class of molecules in which a mechanical force induces a chemical transformation. Because spiropyrans are also chromophores, it is possible to visualize the switching event. The mechanical rupture of the bond between the spiro carbon atom and the oxygen atom can be induced by grinding of the solid spiropyran [2]. The use of spiropyrans as mechano active sensors in materials (such as polymers) requires a covalent connection of the mechanophore to polymeric chains [1]. This construction principle enables the material to

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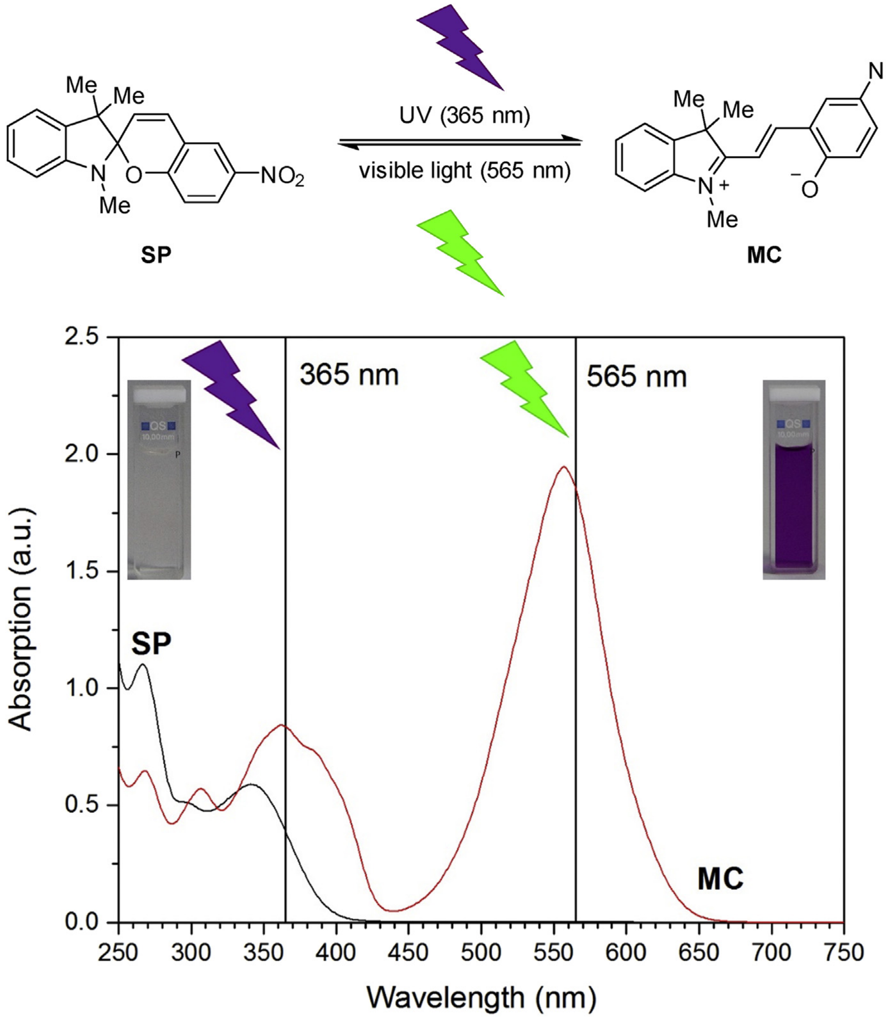

**Fig. 1.** top: Switching states of spiropyrans. The closed spiropyran form (**SP**) undergoes a ring opening upon irradiation with UV light (365 nm, purple flash) to the open merocyanine form (**MC**). Irradiation with visible light (565 nm, green flash) induces a ring closure and drives the equilibrium towards the **SP** side. Bottom: Absorption spectra and photographs of the two states. The absorption spectrum of the **SP** is plotted in black, the spectrum of the **MC** in red. Flashes and vertical lines represent the wavelengths used for switching. Whereas the colorless SP form does not absorb at wavelengths higher than 400 nm, the solution of **MC** shows a dark purple color which results from a broad absorption with a maximum wavelength of approx. 550 nm. The solution in acetonitrile had a concentration of 65 μmol/L and irradiation times of 30 s were used. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

respond to stretching or compression by a color change [6].

Thus, mechanical forces applied to the periphery of the molecule are being transferred to the central bond. DFT calculations suggest a functionalization of the spiropyran at both, the chromene and the indole side, which was confirmed experimentally [14]. However, the possibilities to access these two positions are very limited. To date, a covalent incorporation of spiropyrans to the backbones of polymers was achieved by six methods: electropolymerization, [24] introduction of an ATRP initiator by ester condensation to a phenolic spiropyran, followed by radical polymerization, [18] polyurethane (PU) formation, [17] hydrosilation, [19] ring-opening polymerization (ROP) with $\varepsilon$-caprolactone, [15] ring-opening metathesis polymerization (ROMP), [21] and polycondensation by Suzuki coupling [25–27]. The incorporation into polysiloxanes by hydrosilation as well as the usage of ATRP, ROP or ROMP methods or polycondensations to form PU use hydroxyl groups at the spiropyran. In contrast, due to a limited availability of spiropyrans with halide functions, very few examples of functionalization of spiropyrans by cross coupling have been reported [25–27]. Especially the differentiating functionalization of the two halves of the molecule (indoline and chromene) with groups of different reactivity promises a broader variety of options for further functionalizations and thus a wider applicability of spiropyrans.

Therefore, to make spiropyrans amenable as electrophiles in cross coupling reactions, a library of spiropyrans was synthesized that contained several substitution patterns of bromide, iodide and trifluoromethanesulfonyl as leaving groups.

## 2. Experimental part[1]

Spiropyrans **1** are typically synthesized by a condensation reaction of a Fischer's base and a salicylaldehyde **2** (Scheme 1, section 2.2.1) [28]. The Fischer's base is released *in situ* from an indolium salt **3** under basic conditions. To establish a general procedure (9 examples) for the versatile functionalization of spiropyrans, it was

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[1] Further information concerning the used chemicals (supplier, purity, and purification procedures), equipment and experimental data (detailed procedures, purification, characterization, NMR spectra) are provided in the supporting material.